1994

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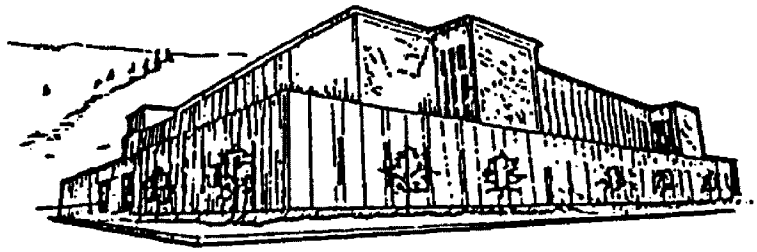
Shawn Gavin Benner
The University of Montana



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Date: May 17 '93

GEOCHEMICAL PROCESSES IN A TRANSITION ZONE BETWEEN SURFACE WATER AND ACIDIC, METAL-RICH GROUNDWATER

by

Shawn Gavin Benner

B.A., The Colorado College, 1988

Presented in partial fulfillment of the requirements
for the degree of
Master of Science
University of Montana
1994

Chairman, Board of Examiners

Dean, Graduate School

May 18, 1994
Date

Benner, Shawn G.,
1994

M.S., Geology

Geochemical Processes in a Transition Zone Between Surface Water and Acidic, Metal-Rich Groundwater

Director: Johnnie N. Moore

This work documents the size, shape and geochemical character of the transition zone between surface water of a small creek and underlying acidic, metal-rich groundwater. Determination of water chemistry combined with a unique *in situ* method of sampling the solid phase chemistry (mineral coatings on installed ceramic beads) allowed me to build an unusually complete picture of the geochemistry during surface/groundwater interaction. The concentrations of metals on the sampled substrate is inversely related to their respective concentrations in the aqueous phase, clearly documenting separation between the solid and aqueous phases. It was found that within the bed sediment of the creek a geochemically-defined transition zone of about 1 meter exists between acidic metal-rich groundwater (pH= 4.5, Fe Conc.= 300 ppm) and relatively clean surface water (pH= 7.9, Fe Conc.= 0.2 ppm). This work has defined the extent of this transition zone geochemically and built a model of the flow system that explains the chemistry found and fits existing hydrologic data. It is possible to achieve the water chemistry composition found in the transition zone by the oxidation of sulfides within the bed sediment by infiltrating surface water, or by a mixing ratio of 96:4 surface water to contaminated groundwater. The behavior of metal contaminants in this system is discussed.

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Acknowledgements

I would like to acknowledge Eric Smart, with whom I conducted a joint project at the Silver Bow Site. Without his energy and expertise, this project would never have been successful. I would like to acknowledge Jim Gannon and Bruce Wielinga for their contribution to the bead-tube concept. I would also like to thank Lynn Biegelsen, for laboratory analysis and Chris Brick, for review and discussion of this manuscript. A big thank you to my committee: Bill Woessner and Garon Smith and especially Johnnie Moore for their knowledge and guidance. A special thanks to Juliana Plater who's support has kept me going, and happy. This work was funded by The Western Mine Land Reclamation Center and the University of Montana.

This Thesis is Dedicated
to My Parents
Joan and Steve Benner

Introduction

The interface between streams and underlying shallow groundwater is increasingly recognized as a distinct biogeochemical environment. Important transformations occur within this zone that can impact the chemical make-up of both the overlying surface and underlying groundwater systems. Ecologists have established the importance of this zone (which they term the hyporheic zone), not only as a biologically rich ecotone, but also as an interface that is important to the entire river's ecology [1]. In coarse-bedded stream channels extensive physical and chemical interaction, between stream water and surrounding sediment pore water, results in a zone of mixing [1-5]. Researchers on the Glatt River in Germany showed that the mobility of many ions changes at the interface between infiltrating surface water and groundwater [6, 7]. Much of this work has suggested that the interactions between the aqueous phase and the substrate play an important role in controlling solute behavior. However, fully understanding ion speciation is often hampered by a lack of knowledge of the solid-phase present. Combining this unique, *in situ*, solid-phase sampling technique with more traditional water sampling and analysis provides an unusually complete picture of the behavior of chemical constituents at this interface in a stream-groundwater system contaminated

with metals.

The production of acidic, metal-rich waters from the oxidation of sulfide minerals found in mine tailings is well documented [8, 9]. These waters often contain high levels of Fe and Mn in addition to elevated amounts of the trace elements As, Cd, Cu, Pb, and Zn. Iron and Mn can precipitate from these waters forming oxide mineral phases. Trace metal contaminants are often associated with these oxides by the processes of coprecipitation and adsorption [10-14]. The oxidation of Fe and Mn to form oxide precipitates is induced by an increase in pH or pE [15].The toxicity of these waters is, in a large part, directly related to the presence of the metals in the aqueous phase [16]. Therefore, understanding the processes controlling metals behavior in waters in natural settings is critical to any meaningful assessment of the impact and remediation of acid mine drainage problems.

Study Site

Silver Bow Creek, located in the headwaters of the Clark Fork River drainage of Western Montana, provides an opportunity to study the geochemical processes at the interface of acidic, metal-rich groundwater and relatively uncontaminated surface water (Figure 1).
Turn-of-the-century mining in Butte, Montana, located 18 km upstream

from the research site on Silver Bow Creek, resulted in the production of large volumes of heavy-metal contaminated waste tailings. Much of these tailings were deposited into the stream bed of Silver Bow Creek. Subsequent floods transported the waste downstream, redepositing it as over-bank floodplain deposits over 100 miles of the Clark Fork River drainage [17]. At the research site, tailings are deposited 1.5 meters thick over a floodplain about 200 meters across (Figure 2). Three hydrostratigraphic units are present. The base of the aquifer (2 to 4 meters below ground surface) is bound by a clay-rich layer of undetermined thickness that is believed to be the weathered layer overlying a volcanic tuff. The aquifer material is approximately 2 meters thick and composed of coarse sand and gravel. The unsaturated zone is zero to 2 meters thick and is composed of a complex stratigraphy of fine to coarse-grained tailings material enriched in As, Cd, Cu, Fe, Pb, and Zn and fine and coarse-grained uncontaminated flood plain deposits [18] (Figure 3). Table I shows representative metal concentrations from sediment at the Silver Bow Creek Site.

At the location of this study, the near-surface aquifer is locally contaminated with acidic, metal-rich water. This contamination is likely the result of the oxidation of sulfides in the vadose zone and the subsequent migration of acidic, metal-rich water downward into the aquifer. The pH is

approximately 4.5, alkalinity is zero and dissolved oxygen less than 1 mg/l. Metal concentrations are high with elevated levels of Cd, Cu, Fe, Mn, and Zn. The chemistry of the groundwater at the site is controlled by the oxidation of organic matter and the flux of acidic metal-rich water from the vadose zone. The resulting water is significantly more reduced and acidic than the surface water [18, work in progress]. Table II shows representative metals concentrations in ground and surface waters.

The water table at the site is between zero and 2 meters below ground surface, depending on topography. Well level response to changes in stream stage, as well as potentiometric maps of the water table, shows that the groundwater and surface water systems are well connected (Figures 2, 3 and 4). These hydrologic data also show that the stream at the Silver Bow Creek is a "flow-through" system with respect to groundwater— when the stream is perpendicular to groundwater flow, groundwater enters the stream on the up-gradient side and exits on the down-gradient side. The study site is located at such a location. Flow direction within the bed sediment of the creek itself is not clearly defined. The measured distribution of hydraulic head suggests that creek water is infiltrating into the bed sediment, and that groundwater is also flowing laterally beneath the creek. Therefore, any mixing zone located under the creek may receive input from the stream channel above or laterally from

groundwater. Water chemistry and flow directions recorded with seepage meters in the up-gradient bank of the creek show that the flow field is variable. At times, contaminated groundwater appears to flow into the creek, at other times, creek water appears to be flowing into the bank.These fluctuations in flow direction are believed to be the result of changing creek stage and resultant changes in flux between the creek and the groundwater. Because there is a slight delay in the response of the groundwater to stream stage, an increase or decrease in stream level will result in a temporary flux of water between the creek and the groundwater. Despite these variabilities in hydrology, I have defined the size and shape of the hyporheic zone underlying Silver Bow Creek and documented the importance of the geochemical processes within this zone in controlling the behavior of metals in the system.

The vast majority of the time the creek water does not exhibit contamination from the nearby tailings. The pH of the surface water is neutral (pH= 7.8). Alkalinity and dissolved oxygen concentrations are high 85 mg/l and 8 mg/l, respectively). Diurnal fluctuations in pH, dissolved oxygen, and temperature have been observed in the surface water of Silver Bow Creek [19]. These fluctuations are likely controlled by respiration and photosynthesis of algae within the stream bed [20, 21]. Metal concentrations in the surface water are low, as expected, given the high pH

and dissolved oxygen levels [18]. Though the stream appears uncontaminated, short periods of high-level contamination do occur. Occasional runoff events lasting on the order of minutes to hours result in an influx of acidic, metal-rich water. This contamination sequence has been documented along the Clark Fork River downstream from Silver Bow Creek [22].

Methods

Field

Water sampling wells and a solid phase sampler were installed into the bed sediment of the creek and the adjacent groundwater (Figure 3). Tubes filled with 2 mm diameter aluminum silicate ceramic beads were installed vertically into the creek bed to collect mineral coatings. Bead-tubes were constructed with 1.75 meter long polycarbonate tubing(3/8 inch OD, 1/4 inch ID) which was slotted (1 mm) on two sides at 1/2 centimeter intervals using a band saw. Beads (2 mm average diameter) were then inserted into the slotted tubing with each bead section (15 cm) separated by a solid piece of polycarbonate rod. The spacers provided divisions for sampling purposes and prevented water from flowing vertically within the bead-tube. The bead-tube was then connected as a

package with a non-slotted tube for additional structural support. This bead-tube set was then acid cleaned in 50% reagent-grade HCl for 1 hour and rinsed repeatedly with sterilized deionized water until a pH of 5 was reached. The bead-tube set was transported in a sterile container to the field site. The tube was installed vertically into the creek bottom by first pounding a 2 inch steel pipe with a solid rod inside into the sediment, then removing the inner steel rod, inserting the bead-tube into the now open pipe and finally removing the pipe, allowing the sediment to collapse back around the bead-tube set. Both bead-tube sets were installed on One bead-tube set was then left in the sediment for 6 weeks, a second for 15 weeks. When each bead-tube set was removed, it was immediately rinsed with sterile, deionized water, cut into 15 cm sections and stored for transport in either an oxic or anoxic chamber depending on the chemical environment of the depth from which they were removed.

During water sampling and collection, every attempt was made to minimize sample contact with oxygen. A small sample volume was removed to avoid averaging and to delineate vertical variation as much as possible. In addition to the bead sites, groundwater access tubes were constructed of 3/8 inch (OD) polyethylene tubing with 5 cm of the tip slotted and covered with a fine mesh screen and installed as a nest. They were placed at 30 cm intervals into the creek bottom using the method

described above for bead-tube installation. Sampling was accomplished using a 60 cc syringe. One tube volume was purged then a sample was taken. Samples were filtered through 0.45 μm filter and acidified with concentrated trace-metal grade HCl to a pH of 2 for cation analysis. Samples for anions were also filtered but not acidified. Alkalinity samples were collected unfiltered and unacidified. Dissolved oxygen and pH were measured immediately upon removal. Though the measured values for dissolved oxygen correlated well with data collected using an enclosed flow-through cell, the sampling method requires that dissolved oxygen values be regarded only as a trend in relative oxygen concentrations. Nested wells were also installed approximately one meter away from the creek to sample groundwater approaching and leaving the creek (Figure 2 and 3). These wells were also sampled as described above. Because of the need to take small sample volumes, it was not possible to purge until chemical parameters were stable or to collect duplicate samples.

Laboratory

Upon arrival in the laboratory, the bead tube sections were dried at 70 degrees Celsius for 24 hours. The beads were removed from each section into a beaker. When present, accumulated algae was removed by gently breaking it off and sieving to separate it. The coatings were

extracted from the beads using aqua regia digest (3:1, hydrochloric: nitric acids). This solution was then analyzed for Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb and Zn using a Thermo Jarrel-Ash Atom-Comp 800 ICP for major cations. These results are reported as μg element/gm of beads. Water samples were analyzed for cations (Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn) using standard techniques on the same ICP. Anions (nitrate, sulfate, chloride) were analyzed using a Dionex 2000 Ion Chromatograph (IC). Water chemistry results are reported in mg/l (ppm). Precision of the ICP analysis was established by the use of duplicates. Duplicates ranged from 97 to 108% for all elements with the exception of Zn, Na and K which ranged from 95 to 122%. Accuracy was established by the use of spikes. Spikes of between 10% and 1000% of analyte were recovered at a range of 104 to 115% for all ions except Zn, Na and K which were recovered at a range of 94 to 117% (Table III). Precision of IC analysis was established by use of duplicates. Duplicates ranged from 99 to 100%. Accuracy was established using spikes. Spikes of between 10 and 500% of analyte were recovered at a range of 98 to 103% (Table IV). Bead blanks exhibited significant concentrations of Al and Si and data for these metals on the beads have been deleted. Bead blanks exhibited insignificant levels of contamination for all other elements. Total alkalinity was determined using a Hach colorimetric technique.

Results and Discussion

Accumulations on the Beads

Given the location of the study (in the bed of a stream) and the nature of the material (coarse sand to cobbles) the collection of representative sediment cores was deemed impractical. In addition, I believe that in some ways the use of the beads are superior to the sampling of sediment cores. An advantage of the use of beads over analysis of sediment is that the beads do not have a history of weathering and coatings accumulation. Extraction and analysis of coatings on grains will necessarily include not only the outer-most layer of the coating present, but all the underlying layers of material as well. These underlying layers are not necessarily in equilibrium with the surrounding water and may be the product of very different geochemical conditions. The complexity of the coating history is only limited by the age of the grain. The use of beads has the potential to eliminate this problem of history because the beads will only reflect the geochemical conditions during the period in which they are in the sediment. However, the beads do have some limitations. The beads themselves do not exactly mimic the physical and chemical characteristics of the natural substrate. The specific mineralogy of the sediment can effect

sorption processes [23].

The rates of accumulation on the beads appear to be different on the 6 and 15 week bead sets. A plot of the % difference between metal concentrations on the 6 and 15 week beads sets shows that there is smaller increase in metal accumulations in the surface water section (40-80% increase) than in the transition zone section (200-900% increase) (Figure 5). The surface water section had already accumulated high levels on the 6 week set (e.g. Fe: 150 µg/gm bead), while the transition zone had only accumulated moderate concentrations (e.g. Fe: 15 g/gm bead). This indicates that the bead section in the surface water may have begun to reach equilibrium with the system during the first 6 weeks. That the rates of accumulation on the beads are different for different depths, is to be expected given the differences in the geochemical environments (See below). This suggests that the rates of accumulation on the beads may not be a reflection of the rates within the surrounding sediment. However, the geochemical controls on the beads are the same as those on the sediment and the processes of sorption on the beads are constrained to processes that also occur on the sediment. I conclude that the presence or absence of constituents on the beads is a reflection of the surrounding sediment and the geochemical factors controlling sorption in that environment.

A Transition Zone

The pH profile of the water within the creek and downward in the sediment clearly defines the depth of the transition zone. The profile shows three distinct zones: Zone 1, from 8 to -8 cm, the pH is ~7.8; Zone 2, from -8 to -80 cm, the pH is ~6.5; and Zone 3, from -80 to -140 cm the pH is ~4.5 (Figure 6). Pore water chemistry in Zone 2, to a depth of 80 cm in the stream bed, is clearly different from both surface (Zone 1) and surrounding groundwater (Zone 3). This water, with a pH of 6.5, average alkalinity of 70 mg/l, and average dissolved oxygen concentrations of 6 mg/l, chemically falls in-between surface and groundwater. This suggests a profile of the ground and surface water interaction composed of two aqueous end members, surface water and contaminated groundwater separated by a zone of intermediate composition, the transition zone.

Metal concentrations in bead coatings on the 6 week bead-tube set correlate well with the above described zones. In general, concentrations of Ca, Cd, Cu, Fe, K, Mg, Mn, Na and Zn in the bead coating are directly related to the pH and inversely related to concentrations of metals in the water. In the groundwater (Zone 3), where metal concentrations are high in the aqueous phase and pH is low (Fe= 350 ppm, pH= 4.5), the concentrations on the beads are low (Fe= 5 g/gm bead). In the surface water and transition zone (Zones 1 and 2), which have low metal

concentrations in the aqueous phase and high pH (Fe: 0.2 ppm, pH= 7.8), concentrations of metals on the beads are high (Fe= 160 g/gm bead). The surface water, with a pH of 7.8, has higher concentrations of metals on the beads than the transition zone, with a pH of 6.5.

Nested wells on the banks of the creek were used to determine the lateral extent of the transition zone. Water from wells located one meter from the up-gradient side (relative to groundwater flow) shows no obvious chemical influences from the creek (Figure 6). The up-gradient bank of the creek is coated with a bright orange crust at the water table. This indicates that precipitation of Fe-oxides is occurring at the pore water-creek contact. Samples of in-flowing groundwater on the up-gradient side of the creek varied in pH from 4 to 7, suggesting a small, but fluctuating, transition zone. The wells located one meter from the down-gradient side of the creek do show influences of the creek; with a pH of 6 and moderately high metals concentrations (Fe=10 ppm). A well located 10 meters away from the creek on the down-gradient side shows no measurable influence of the creek (pH= 4, Fe= 360 ppm). These wells constrain the transition zone to less than one meter on the up-gradient side and at least one, but less than 10, meters on the down-gradient side. The lateral extension of the transition zone is clearly influenced by the regional groundwater flow field.

Transition zone boundaries

Within the vertical profile, the boundary between the surface water and the transition zone is gradational. Water chemistry at -10 cm depth is very similar to surface water but at -30 cm depth the water is clearly different. The gradational nature of the upper boundary of the transition zone is in agreement with a model of stream-pore water interaction proposed by [24]. They examined physical mixing using tracers and found that surface water interacted extensively with the shallow gravel bed and, to a lesser degree, with deeper alluvium. This work provides chemical evidence for similar behavior. Alkalinity and pH of the water in the upper 10 cm of the bed sediment beneath the creek are very similar to surface water, suggesting extensive interaction. Below 10 cm, and to a depth of 80 cm, pore water is considerably more acidic and less buffered, but still exhibits obvious influences from surface water. The coarse-grained bed material results in high rates of exchange of surface water with the shallow bed sediment pore water.

The boundary between the transition zone and flood plain groundwater is more distinct. Metal concentrations in the water vary by as much as three orders of magnitude over a distance of less than 20 cm. The 6 week bead set exhibits high concentrations of Fe at this contact. Visual

evidence in the form of orange coatings on the beads at the -80 cm mark suggests that this contact is less than 5 cm in width. These chemical data, which indicate abrupt contact between the transition zone and groundwater, can be used to construct a tentative model of the physical flow field. Given the large chemical signature of the surface water in the transition zone, it is clear that there is some component of downward flow. It is difficult to picture producing the chemical profile of the lower boundary of the transition zone by gradational dilution or mixing. Therefore, I propose that the downward component of flow apparently dissipates by the time the downward migrating surface water reaches the -80 cm depth. At that point the water in the transition zone is moving parallel to the flood plain groundwater system (Figure 8). This model fits existing hydraulic head data at the site (Figure 3).

Based on my sampling scheme, there is also evidence that the lower boundary of the transition zone fluctuates. The metals profile of the 15 week bead set is essentially the same as the 6 week bead set but appears to indicate a much smaller transition zone. The 6 week bead set shows a zone of accumulation from the surface (zero cm depth) to the -82.5 cm depth. This correlates well with the defined transition zone. On the 15 week bead profile this zone of accumulation only extends to the -52.5 cm depth. This may be attributed to lateral variability because the 15 week bead set was

located about 1.5 meters away from both the 6 week bead set and the water sampling wells. But, it is also possible that at the time of the removal the transition zone was smaller. This can be explained by fluctuations in the location of the boundary between the transition zone and the contaminated groundwater. A lowering of the stream stage would result in a temporary increase in the flux of water from the groundwater to the stream which would result in a reduction in the thickness and extent of the transition zone. A fluctuating contact between the contaminated groundwater and the transition zone will limit the amount of metals that accumulate in the lower part of the transition zone. Changes in the location of this boundary would result in periodic influxes of acidic groundwater from below. This would dissolve any accumulated sorbed material. Therefore, though the lower boundary of the transition zone appears to be an area of rapid sorption, it may not be a zone of major accumulation. The amount and location of coatings on the beads at this lower interface may reflect a very short period of accumulation, and therefore should be considered a "snapshot" of metals behavior at the time of removal.

Metals Behavior

The behavior of metals within surface, transition zone, and groundwater systems is controlled by geochemical conditions of the

aqueous phase. Relative concentrations of metals on the beads and in the aqueous phase appear to fit well with previously established theoretical and field-recorded behavior.

Iron: The presence of extensive Fe rich coatings on stream sediment indicates that Fe is precipitating as Fe oxides in the stream [25, 26] . High Fe concentrations throughout the transition zone indicate that precipitation of Fe oxides is occurring to a depth of -80 cm. Below this point Fe is not undergoing sorption, and Fe concentrations are high in the aqueous phase. This suggests that the contact between the transition zone and groundwater is also the geochemical boundary for Fe. Above the boundary, the dominant Fe species is Fe-oxides and below the boundary the dominant species is the soluble form (Fe^{2+}). This fits well with theoretical Eh-pH diagrams of the Fe system [15]. Eychaner (1991) [13] found Fe^{2+} oxidized and precipitated as Fe-oxyhydroxides at a pH of 5 during dilution of acidic metal-rich groundwater, which is in agreement with Fe behavior in this study. Iron concentrations in the water at a pH of 4.5 are high (350 ppm) while in water of a pH of 6.5, Fe concentrations are low (0.5 ppm). In the sediments of Silver Bow Creek, this gradient may be induced by a change in redox potential, pH or a combination of the two, since both parameters decrease with depth. The beads show a concentration maximum for Fe at the contact between the transition zone and the groundwater. High Fe

concentrations at this contact can also be explained by precipitation of iron oxyhydroxides and suggests that this concentration maximum reflects a zone of mixing between transition zone water and metal-rich groundwater.

Manganese: Manganese shows high levels of accumulation on the beads in the surface water, but little or no accumulation on the beads in the transition zone and contaminated groundwater.Manganese is present in the aqueous phase in the groundwater and transition zone at elevated levels relative to the surface water. The speciation boundary between Mn oxides and soluble Mn (Mn^{2+}) correlates well with the boundary between the surface water and the transition zone water. Above this boundary, Mn oxides are the dominant phase and below this boundary Mn^{2+} is the dominant phase. Mn-oxides theoretically precipitate under conditions more oxic and basic than Fe-oxides [15]. A similar relationship to Fe with respect to redox gradient has been documented in the field [27 , 28]. Like Fe, this gradient can be induced by decreasing redox potential or pH.

Trace Metals: Based on the relatively high concentrations of As, Cd, Cu, Pb and Zn in the coatings compared to the aqueous phase, these elements appear to be primarily partitioned in the solid phase. The removal of these elements may be the result of the precipitation of solid phase minerals or they may also be removed from the aqueous phase by adsorption on iron oxihydroxides. The degree of adsorption of a given

cation to iron oxyhydroxide is primarily dependent on pH and the relative concentrations of the cation and adsorbing sites. In this case the number of adsorbing sites is not known. Nevertheless, for a wide spectrum of site densities, laboratory-determined adsorption isotherms for these three elements are located in a pH range from 4.5 and 6.5, the same pH range as the transition zone [29]. Adsorption of these ions at similar pH values has been documented in the field [12, 30].

Other Major Elements: Given that the surface water concentrations of Ca and Mg are higher than the concentrations found in the transition zone water, these two elements must be undergoing sorptive removal from the infiltrating surface water. This is confirmed by high Mg and Ca concentrations (Ca= 40 g/gm bead, Mg= 10 g/gm bead) on the beads in the transition zone. Since pH decreases downward, it is difficult to evoke an adsorption edge threshold model. A possible explanation is that the adsorption edge for these two ions is below a pH of 6 and that the change in concentrations in the water is the result of an increase in adsorption site density in the transition zone. The pore water in the transition zone is in contact with more adsorption sites and therefore Ca and Mg are more likely to be adsorbed. As a result, as surface water infiltrates into the transition zone, Ca and Mg concentrations go down. While Ca and Mg concentrations decrease, the concentrations of the monovalent cations Na

and K show only a small decrease and only low levels of accumulation on the beads. This suggests an adsorption preference for divalent cations.

Alkalinity: The profile of alkalinity concentrations in the water mimics the profile of pH. It is likely that alkalinity is being consumed by acid from the oxidation of sulfides or mixing with groundwater. Alkalinity acts to buffer changes in pH. The ability to buffer acidic input is lost when HCO_3^- is converted to H_2CO_3. The equivalence point for these two carbonate species is at a pH of 6.37. Therefore, as the pH approaches and drops past 6.37, the alkalinity is quickly lowered to zero. Like Fe, the transition for alkalinity speciation appears to correlate with the lower boundary of the transition zone.

Oxygen and Nitrate: Dissolved oxygen and nitrate levels within the transition zone water show gradational decrease with depth. Oxygen and nitrate concentrations are likely being lowered by the oxidation of organic matter and/or sulfides. In many systems, surface water infiltrating groundwater often becomes more reduced with depth. The deeper the water is in the transition zone, the longer the residence time and the longer the process of reduction. Therefore, the deeper water would be expected to have lower oxygen and nitrate levels concentrations.

Two conceptual models

We propose two different possible mechanisms to achieve the chemical composition of the water in the transition zone. First, the transition zone water can be produced by mixing of surface and groundwater. Second, the transition zone water may be the product of altered surface water. Given the flow model proposed in Figure 8, the amount of mixing between surface and groundwater below the stream will be limited. Though the flow lines indicate no mixing, dispersion and flow field fluctuations are likely to provide some degree of interaction between the two zones. Though it is not known if any ions in this system behave conservatively, calculating mixing ratios from ion concentrations in the surface and groundwater still proves useful (Table V). These calculations were done using the equation:

$$x = 100\,(C_t - C_{sw}) / (C_{gw} - C_{sw}),$$

where C_{sw} = concentration of constituent in surface water, C_{gw} = concentration of constituent in the groundwater, C_t = Concentration in transition zone water, and x = the percent of groundwater in the transition zone water. Constituents with negative (-) values, have concentrations in the transition zone that are higher than the surface water. For these constituents, the percent calculated is meaningless. Mixing ratios provide a

general sense of the amount of mixing and an indication of the degree of non-conservative behavior. Chloride has been used as a natural, conservative tracer in surface-groundwater interaction [4, 31]. Chloride does appear to behave the most conservatively of all ions measured. Mixing ratios based on chloride indicate that the lower transition zone water (-20 to -80 cm depth) is composed of about 6% groundwater and 94% surface water (Table V). It should be noted that if chloride is not behaving conservatively the percent of groundwater contributed would be even smaller. In addition, of the metals analyzed on the beads, Mn appears to behave the most conservatively with less than 1.5 g/gm bead accumulated and a corresponding aqueous phase concentration of about 2 ppm. Mixing ratios calculated from Mn concentrations in the waters indicate 4% groundwater and 96% surface water which is in good agreement with the Cl numbers.

It is possible to calculate the degree to which a given constituent is depleted in the transition zone water relative to the concentration expected given only conservative mixing. These calculations were done using the equation;

$$y = 100\,(1 - \{Ct \;/\; [0.95(C_{sw}) + 0.05(C_{gw})]\})$$

where C_{sw} = concentration of constituent in surface water, C_{gw} =

concentration of constituent in the groundwater, C_t= concentration of constituent in transition zone water, and y = the percent the constituent is depleted relative to the concentration predicted by conservative mixing. This number ("Percent Depleted", Table V) reflects the degree of non-conservative behavior (sorption) for that constituent.

For example, while Fe and Cu (-99 and -70%, respectively) show a high degree of non-conservative behavior, K and Na (-12 and -7%, respectively) exhibit depletion near the error of measurement and are considered to be acting conservatively. The relative degree of non-conservative behavior by all elements during mixing (Fe > Cd > Cu > Zn > Ca > Mg > Mn) correlates well with the relative amount accumulated on the beads (Fe > Cu > Zn > Ca > Mg > Mn > Cd). Only Cd does not correlate well and this can be attributed to the large error associated with the measurement of the near-detection level concentrations throughout the system.

I also compared the amount contributed by the surface water ($0.94(C_{sw})$) and groundwater ($0.06(C_{gw})$) with the amount found in the transition zone. If the calculated amount contributed by the groundwater or surface water is greater than the total actually found in the transition zone water, metals are being removed from that portion. Calculated concentrations of Cd, Cu, Fe, Mn, and Zn in the groundwater portion are

all higher than those found in the transition zone and therefore, all these elements must be undergoing removal from the groundwater portion. Calculations also indicate that Ca and Mg are undergoing removal from the surface water portion. Though most elements show good internal agreement with the mixing model, sulfate is a notable exception. Sulfate shows a high degree of depletion relative to conservative mixing (44%). If SO_4^{2-} in the transition zone is the product of mixing, a large amount of SO_4^{2-} is unaccounted for.Bigham (1990) [32] found that "amorphous iron oxyhydroxide" may actually be a "poorly crystallized oxyhydroxysulfate of iron." Though it is not known if this sulfate-containing mineral precipitates at a pH range of 4 to 6, formation of such a mineral would help account for apparent non-conservative behavior of sulfate.

Since the degree of mixing indicated to form the transition zone water chemistry is very small and within the error of measurement for many constituents, it seems possible that mixing may not be occurring. We propose a mechanism to achieve the chemical composition within the transition zone without mixing. Water infiltrating into the groundwater often undergoes some degree of reduction [6, 7, 33, 34]. The reaction sequence for the reduction of groundwater is well documented [35] (Figure 9, Reactions 1 - 5). The partial reduction of oxides of Mn and Fe could

produce the increases in concentration from the surface and transition waters in Fe (0.2 to 0.4 ppm) and Mn (0.8 to 2.5 ppm). However, this is unlikely for two reasons. First, the reduction of Fe seems unlikely given the oxygen and nitrate concentrations present in the water. Second, the reduction of nitrate, Mn-oxide and Fe-oxide results in the consumption of H+ ions which will raise the pH. The pH of the transition zone water is, however, lower than the surface water. The pH can be lowered by the production of CO_2 from the oxidation of organic matter, but this will not result in the decrease in alkalinity found in the transition zone (Figure 9, Reactions 6 - 7). In these reduction reactions the main reductant that is being oxidized is assumed to be organic matter (CH_20) but it is also entirely possible for sulfides to be oxidized. The oxidation of sulfides, as represented by the well known pyrite oxidation sequence in Figure 9 (Reactions 9 -12), will result in an increase in metal concentration and a decrease in pH. Given the presence of oxygen and nitrate, this reaction is more thermodynamically favored in the transition zone than the reduction of Mn and Fe oxides. Sulfides are present within the bed sediment of the Clark Fork drainage [26]. The oxidation of these sulfides is presumably limited by encasement in reaction rims of oxides and the kinetics of the oxidation reaction. It is probable, however, that some degree of oxidation

of sulfides in the bed sediment is occurring. Given the higher levels of water-sediment interaction in the pore waters underlying the creek, the transition zone is more likely to show the effects of that oxidation. The oxidation of sulfides of Fe, Cu, Zn, As, and Pb will result in the mobilization of "free" metal ions. These ions may stay in solution in the transition zone, or be removed from the aqueous phase by sorption. This is reflected in the water or bead coating chemistry in the transition zone. The oxidation of sulfides also produces acid which can explain the decrease in pH and alkalinity between the surface and transition zones.

At the base of the bead coating concentration profiles there are high values for a number of metals. Given the lack of oxygen in the groundwater, it seems unlikely that oxides could be forming at this depth.These high metal concentrations on the beads may be the result of sulfide formation. Though the water chemistry does not indicate that metals are precipitating from the groundwater at this depth (i.e. the soluble concentrations are not lower), a profile of bacterial populations shows the presence of sulfate reducing bacteria at this depth [36]. This suggests that sulfides are forming at this depth, perhaps at rates that do not significantly alter the soluble concentrations.

Conclusions

I have documented the size, shape and geochemical character of the transition zone between surface water of a small creek and underlying acidic, metal-rich groundwater. The addition of solid phase data has greatly enhanced physical and geochemical conceptual models of the interface between the surface and groundwater systems. The concentrations of metals on the sampled substrate is inversely related to their respective concentrations in the aqueous phase, clearly documenting speciation between the solid and aqueous phases. I have defined the extent of this transition zone geochemically and built a model of the flow system that fits existing hydrologic data. I found that, within the bed sediment of the creek, a geochemically-defined transition zone of about 1 meter exists between acidic metal-rich groundwater (pH= 4.5, Fe= 300 ppm) and relatively clean surface water (pH= 7.9, Fe= 0.2 ppm). Two models have been proposed to explain the chemical composition of this transition zone water. It is possible to achieve the water chemistry composition found in the transition zone by infiltrating surface water oxidizing sulfides within the bed sediment, or by mixing with ~6% contaminated groundwater. The behavior of contaminants across this transition zone is strongly controlled by a pH and redox gradient between the surface and groundwater systems.

Tables

Table Captions

Table I

Representative sediment chemistry from 5 different test pits at the Silver Bow site. Data were attained by using a partial HCl extract which approximates metal concentrations available to the environment (Luoma and Davis, 1983). Concentrations are in µg/gm sediment.

Table II

Representative water chemistry from well nest in the creek, August 1, 1993. Well depth refers to depth below ground surface. Well depth (8 cm) is surface water. All concentrations are in mg/l.

Table III

ICP level of detection and duplicate and spike recovery data.

Table IV

IC level of detection and duplicate and spike recovery data.

Table V

Mixing ratio calculations between surface water and "average" groundwater to achieve "average" transition zone water. "% GW" indicates amount of groundwater that would need to be mixed with the surface water to achieve the concentration of that constituent. "Percent Depleted" indicates the % of each constituent that must be removed to achieve the concentrations found under the assumption of 5.58% groundwater contribution (based on Cl mixing ratio). "SW*.9442" and "GW*.0558 indicate the amount contributed by the surface water and groundwater, respectively, during conservative mixing.

Table I

Spl#	TP1-6	TP17-1	TP13-1	TP12-2	TP14-4
Ag	5	BDL	10	BDL	2
Al	538	3432	2424	1320	1416
As	111	18	195	BDL	168
Ca	781	12400	3992	1696	461
Cd	1	2	5	1	BDL
Cu	1614	48	2167	141	101
Fe	4848	1448	20800	3856	52720
K	282	2740	559	675	230
Mg	134	6224	676	387	53
Mn	109	464	967	337	46
Mo	9	2	34	6	76
Na	30	260	99	158	40
P	296	512	1440	528	272
Pb	250	22	976	BDL	155
Si	808	5624	3384	1312	1584
Zn	361	348	1178	603	132

Well Depth (cm)	8	-8	-38	-68	-98	-128	-158
Temp	12.4	12.7	13.7	12.5	11.7	11.7	11.9
pH	7.84	7.73	6.94	6.62	4.39	4.59	4.4
D.O.	8.1	7.3	5.5	3.3	2.2	1.1	1.1
Alk.	88	94	72	56	0	0	0
Al	0.143	BDL	BDL	BDL	44.9	24.3	30.3
Ca	45.5	45.2	40.9	37.6	114	143	166
Cd	BDL	BDL	0.0083	0.0086	0.5208	0.5119	0.6104
Cu	0.1035	0.1511	0.5947	0.0993	26.12	13.94	17.31
Fe	0.254	0.305	0.104	0.388	332	355	408
K	4.27	4.33	4.188	4.145	10.73	12.49	13.64
Mg	9.97	9.87	9.27	8.31	30.2	33	37.3
Mn	0.8102	0.7988	1.137	2.678	25.53	28.05	30.77
Na	23.3	23.2	22.9	22.4	39.7	44	44.2
Ni	BDL	BDL	BDL	BDL	0.212	0.264	0.254
Si	14	13.8	12.7	11.1	40.5	38.9	36.4
Zn	0.7401	0.6544	1.374	3.354	41.94	57.28	62.93
Cl	13.2	13.4	13.7	13.5	19.5	2.1	21.5
Nitrate	1.5	1.4	1.5	1.1	BDL	BDL	BDL
Sulfate	67.4	69	74.1	89.5	1412.2	1383.7	1663.9

Element	Level of Detection (ppm)	Duplicates			Spike Recovery		
		Mean	n	Standard Deviation	Mean	n	Standard Deviation
Al	0.12	103%	6	9.1%	106%	9	2.0%
Ca	0.03	103%	8	5.0%	112%	13	3.3%
Cd	0.01	104%	7	5.0%	115%	13	6.1%
Cu	0.02	99%	8	6.6%	106%	13	2.2%
Fe	0.03	97%	8	7.2%	107%	13	3.4%
K	0.75	122%	4	15.7%	109%	13	2.3%
Mg	0.14	105%	8	5.7%	105%	13	1.5%
Mn	0.01	101%	8	5.1%	107%	13	2.7%
Na	0.06	95%	8	3.9%	94%	13	2.0%
Si	0.04	108%	8	9.7%	104%	13	2.2%
Zn	0.01	101%	8	10.3%	117%	13	2.3%

Table IV

Anion	Level of Detection	Duplicates		Spike Recovery	
		Mean (n=6)	Standard Deviation	Mean (n=7)	Standard Deviation
Chloride	5.0 ppm	100.16%	0.33%	103.24%	4.35%
Nitrate	0.75 ppm	99.45%	0.28%	98.29%	4.01%
Sulfate	6.0 ppm	99.26%	5.56%	100.41%	1.37%

Table V

Water	Al	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Si	Zn	Cl	NO2	SO4
Surface water	0.14	45.50	0.00	0.10	0.25	4.27	9.97	0.81	23.30	14.00	0.74	13.20	1.50	67.4
Ave. Groundwater	33.17	141.0	0.55	19.12	365.0	12.29	33.50	28.12	42.63	38.93	54.05	20.37	0.00	1487
Ave.Trans. Water	0.00	39.25	0.01	0.35	0.25	4.17	8.79	1.91	22.65	11.90	2.36	13.60	1.30	81.8
% Groundwater	-0.43	-6.54	1.54	1.28	0.00	-1.29	-5.01	4.02	-3.36	-8.42	3.05	5.58	13.33	1.01
Percent Depleted	-100	-22.8	-72.4	-70.2	-98.8	-11.7	-22.1	-18.3	-7.1	-22.7	-36.4	0.0	-8.2	-44.2
sw(.94)	0.14	42.96	0.00	0.10	0.24	4.03	9.41	0.76	22.00	13.22	0.70	12.46	1.42	63.6
gw(.06)	1.85	7.87	0.03	1.07	20.37	0.69	1.87	1.57	2.38	2.17	3.02	1.14	0.00	83

Figures

Figure Captions

Figure 1
Site Location Map

Figure 2
Site and Potentiometric map: This map shows the location of the study site cross section and a potentiometric map of "semi-steady-state" conditions on July 1, 1994. Groundwater contour intervals (dashed lines) are 0.15 meters. The potentiometric map for the site is highly responsive to fluctuating stream stage.

Figure 3
Cross-sectional profile of groundwater flow net, stratigraphy, instrumentation. Flow net was constructed assuming a horizontal hydraulic conductivity two orders of magnitude greater than the vertical hydraulic conductivity and is based on data collected on April 27, 1994. This flow net is believed to represent "semi-steady state" conditions. Contour intervals are 0.02 meters. Stratigraphy: Unit A = unsaturated zone composed of metal-rich mine tailings and uncontaminated material of fine and coarse sand, Unit B = Sand and gravel aquifer, Unit C = clay confining layer. Instrumentation: WN = well nest, BS1 = 6 week bead set, BS2 = 15 week bead set.

Figure 4
Hydrographs for surface and groundwater. Data plotted to show the delayed response of the groundwater to changes in surface water stage. When surface water levels are going up groundwater levels are relatively lower than the surface water and as surface water levels drop, groundwater levels are relatively higher. Data from Steven's Recorders in stream and in the groundwater.

Figure 5
Vertical profile graph of percent difference in metals (Cu, Fe, Mn, and Zn) between the 6 week bead set (BS 1) and 15 week bead set (BS 2).

Figure 6
Cross-sectional profile of pH values and Fe concentrations in the water. Hash marked area defines transition zone. Transition zone chemistry is intermediate between surface and groundwater. Vertical exaggeration used to show vertical differentiation.

Figure 7a

Vertical profile within the bed sediment of Silver Bow creek of general chemical parameters (pH, Dissolved oxygen, Total alkalinity, and Nitrate) in the aqueous phase. Vertical axis is depth below ground surface, horizontal axis is concentration of each constituent. Dashed lines show geochemically defined divisions between surface water, transition zone water, and groundwater. Oxygen values are shown to represent trends only.

Figure 7b

Vertical profile within the bed sediment of Silver Bow creek of acid mine drainage associated contaminants (Fe, Cu, Cd, Zn, and Mn) in the aqueous phase (A), as coatings on the 6 week bead set (B), and as coatings on the 15 week bead set (C). Vertical axis is depth below ground surface, horizontal axis is concentration of each constituent. Note that the scale on the horizontal axis varies between plots. Dashed lines show geochemically defined divisions between surface water, transition zone water, and groundwater. The accumulations of the 15 week bead set (C) indicate a smaller transition zone.

Figure 7c

Vertical profile within the bed sediment of Silver Bow creek of non-contamination related elements (Ca, K, Mg, and Na) in the aqueous phase (A), as coatings on the 6 week bead set (B), and as coatings on the 15 week bead set (C). Vertical axis is depth below ground surface, horizontal axis is concentration of each constituent. Note that the scale on the horizontal axis varies between plots. Dashed lines show geochemically defined divisions between surface water, transition zone water, and groundwater. In the aqueous phase, all elements show slightly lower levels in the transition zone (A). Ca and Mg show significant levels of accumulation on the beads (B and C).

Figure 7d

Vertical profile within the bed sediment of Silver Bow creek of non-contamination related elements (Cl, Si, Al, and SO_4) in the aqueous phase that were not found or measured for on the beads. Vertical axis is depth below ground surface, horizontal axis is concentration of each constituent. Note that the scale on the horizontal axis varies between plots. Dashed lines show geochemically defined divisions between surface water, transition

zone water, and groundwater.

Figure 7e

Vertical profile within the bed sediment of Silver Bow creek of contamination related elements (As and Pb) in the coatings that were not found in the water. Vertical axis is depth below ground surface, horizontal axis is concentration of each constituent. Note that the scale on the horizontal axis varies between plots. Dashed lines show geochemically defined divisions between surface water, transition zone water, and groundwater.

Figure 8

Cross-sectional profile of physical flow field model. Hashed area marks the transition zone. This is a chemically defined flow field that fits with existing hydrologic data.

Figure 9

Important chemical reactions.

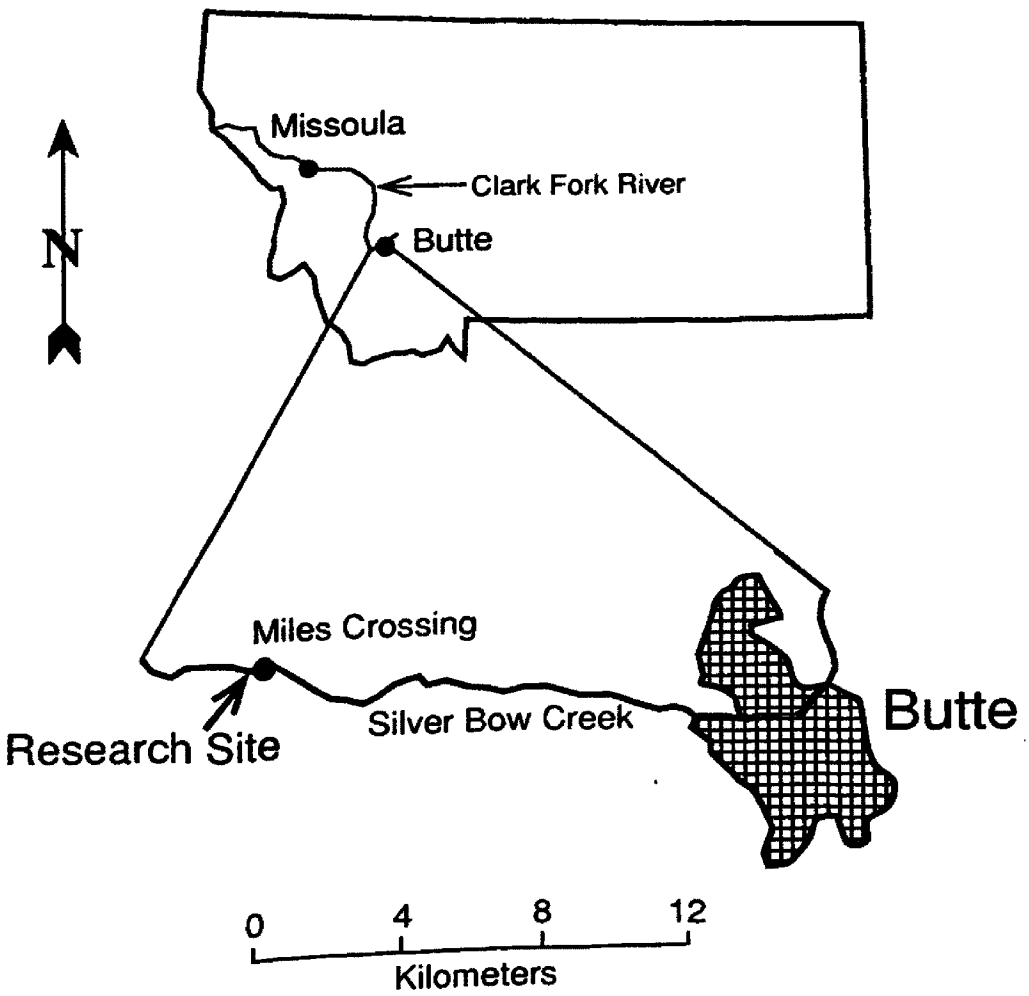


Figure 2

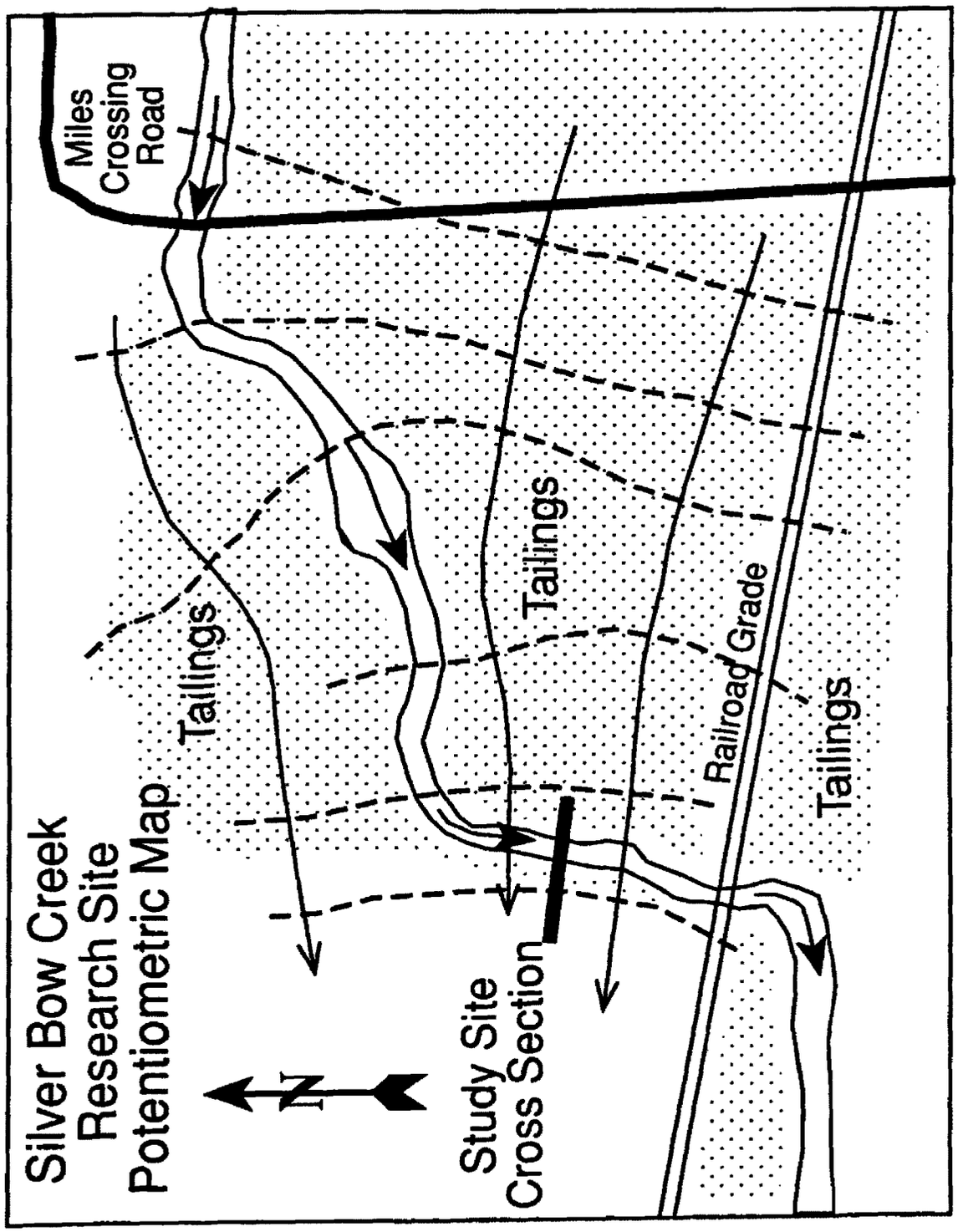
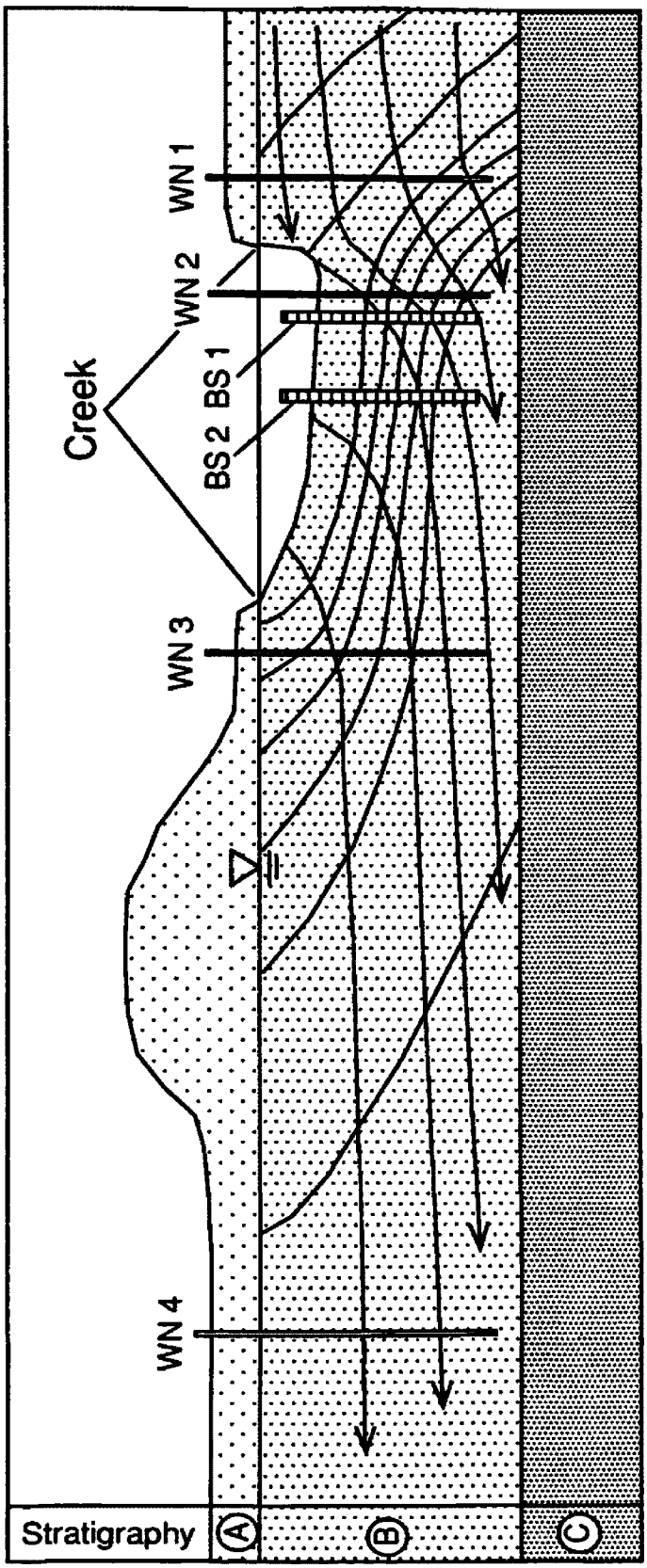


Figure 3



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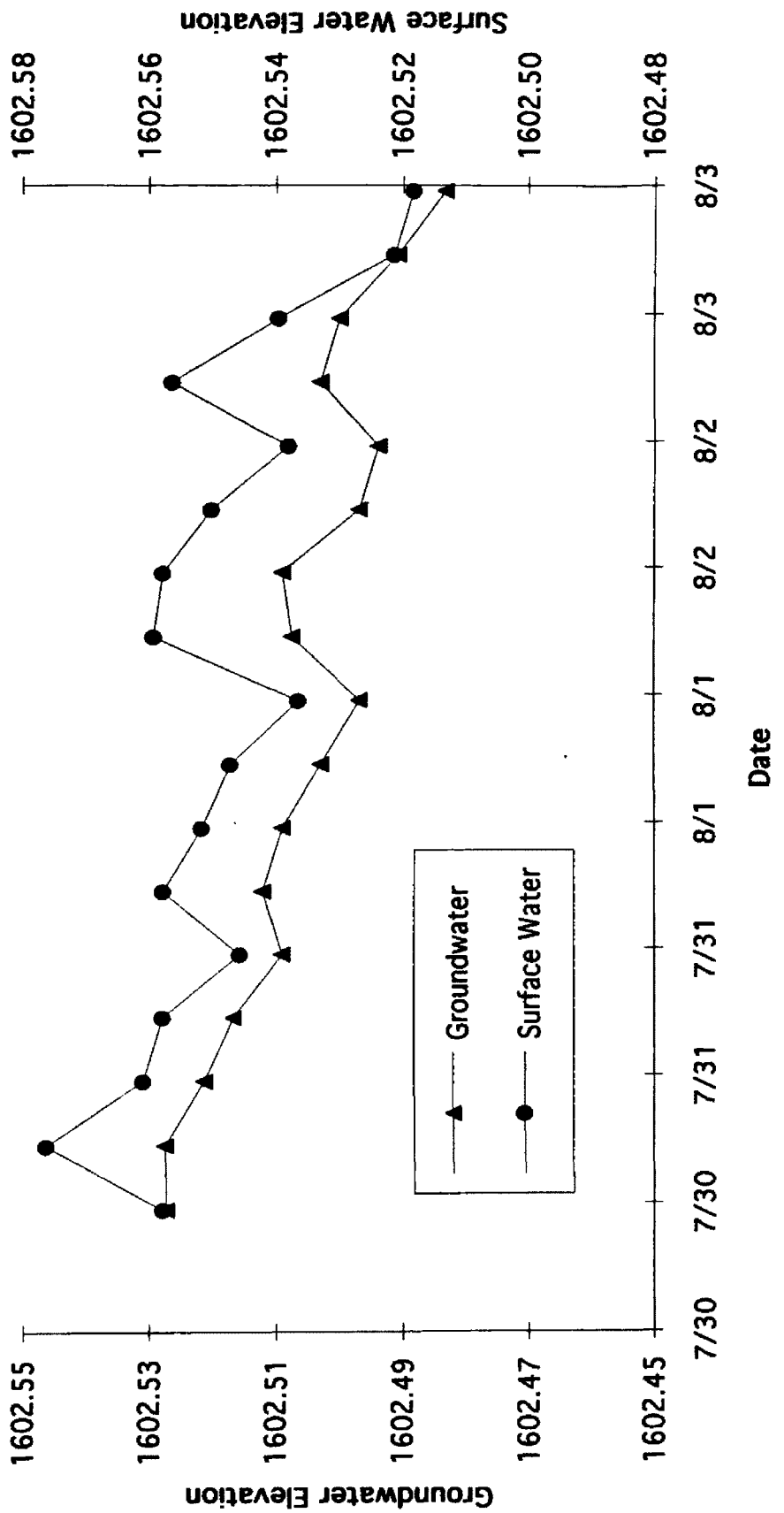


Figure 5

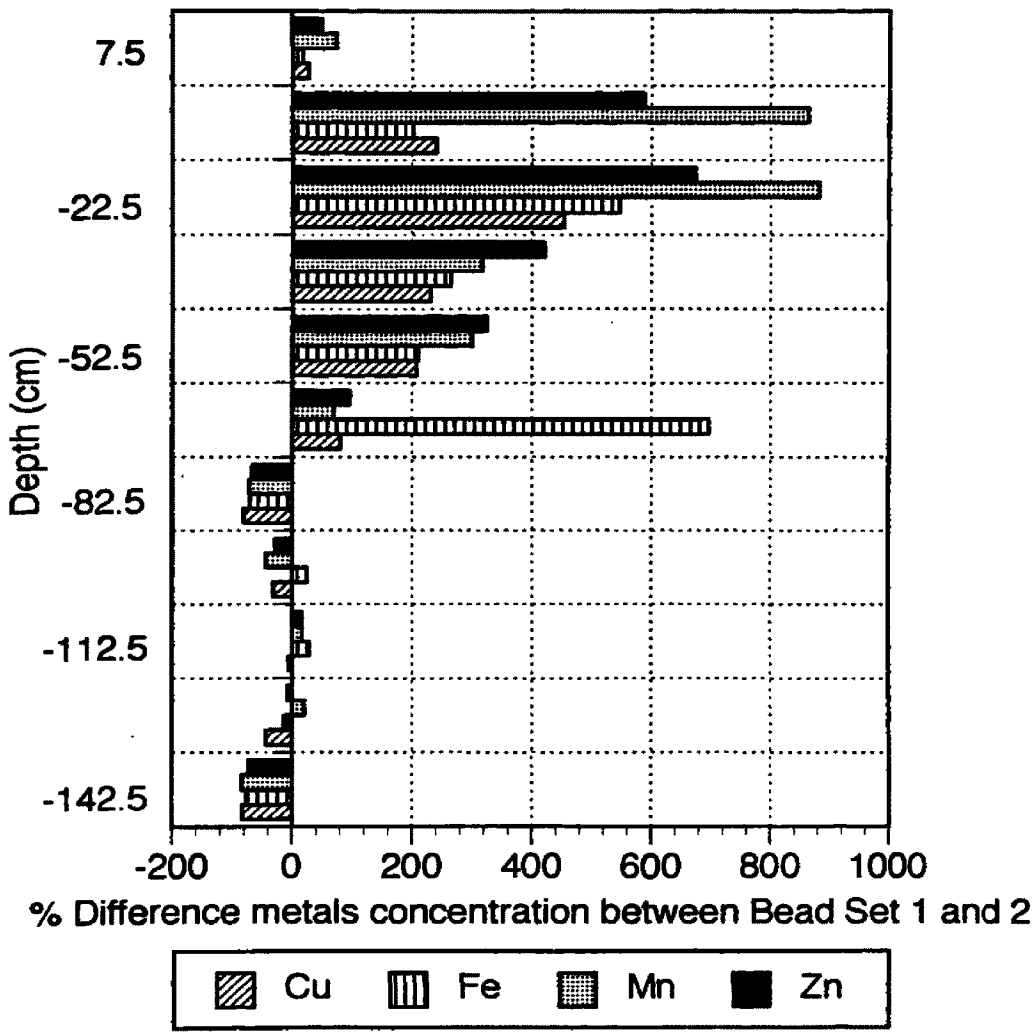


Figure 6

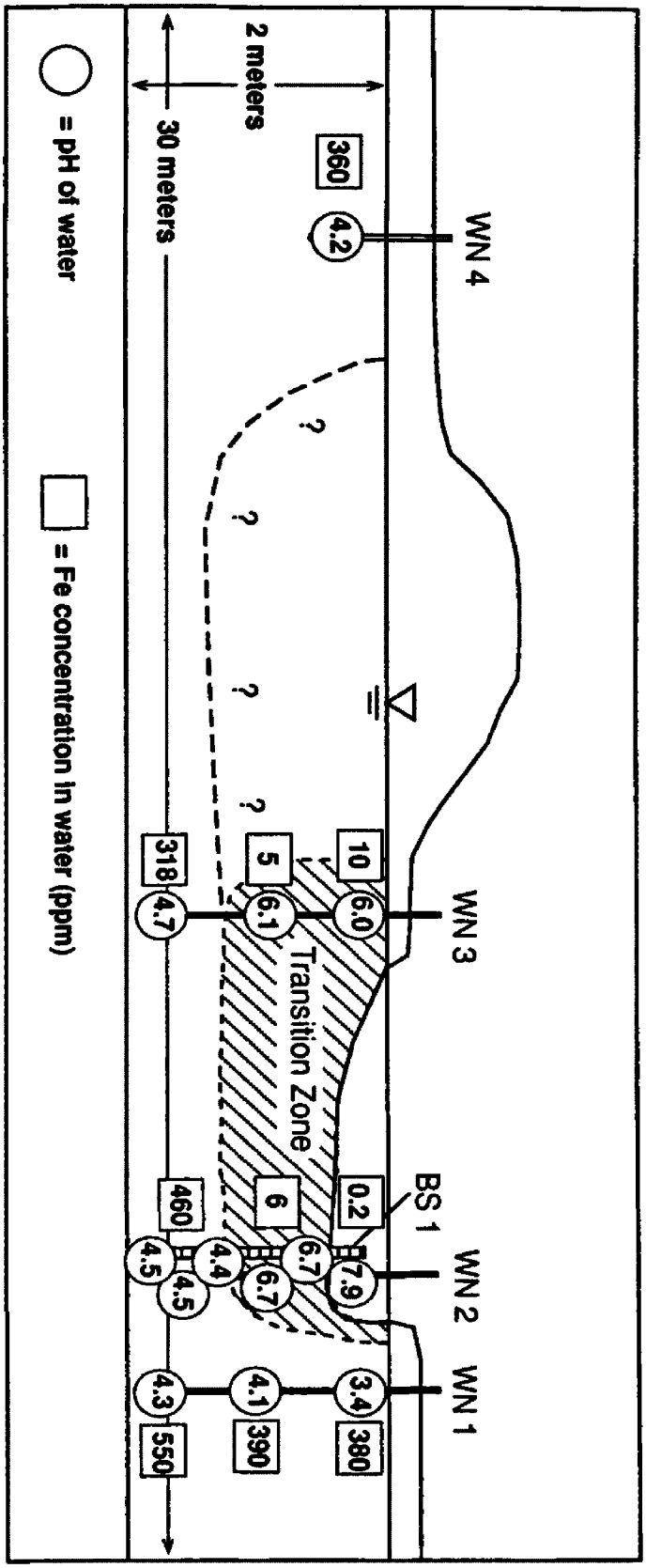


Figure 7a

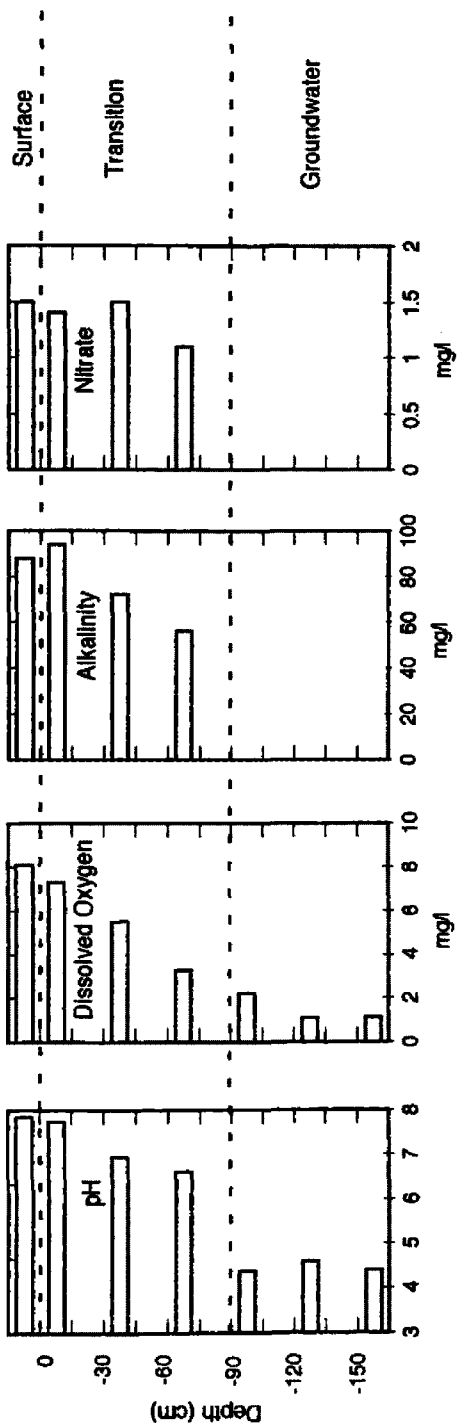
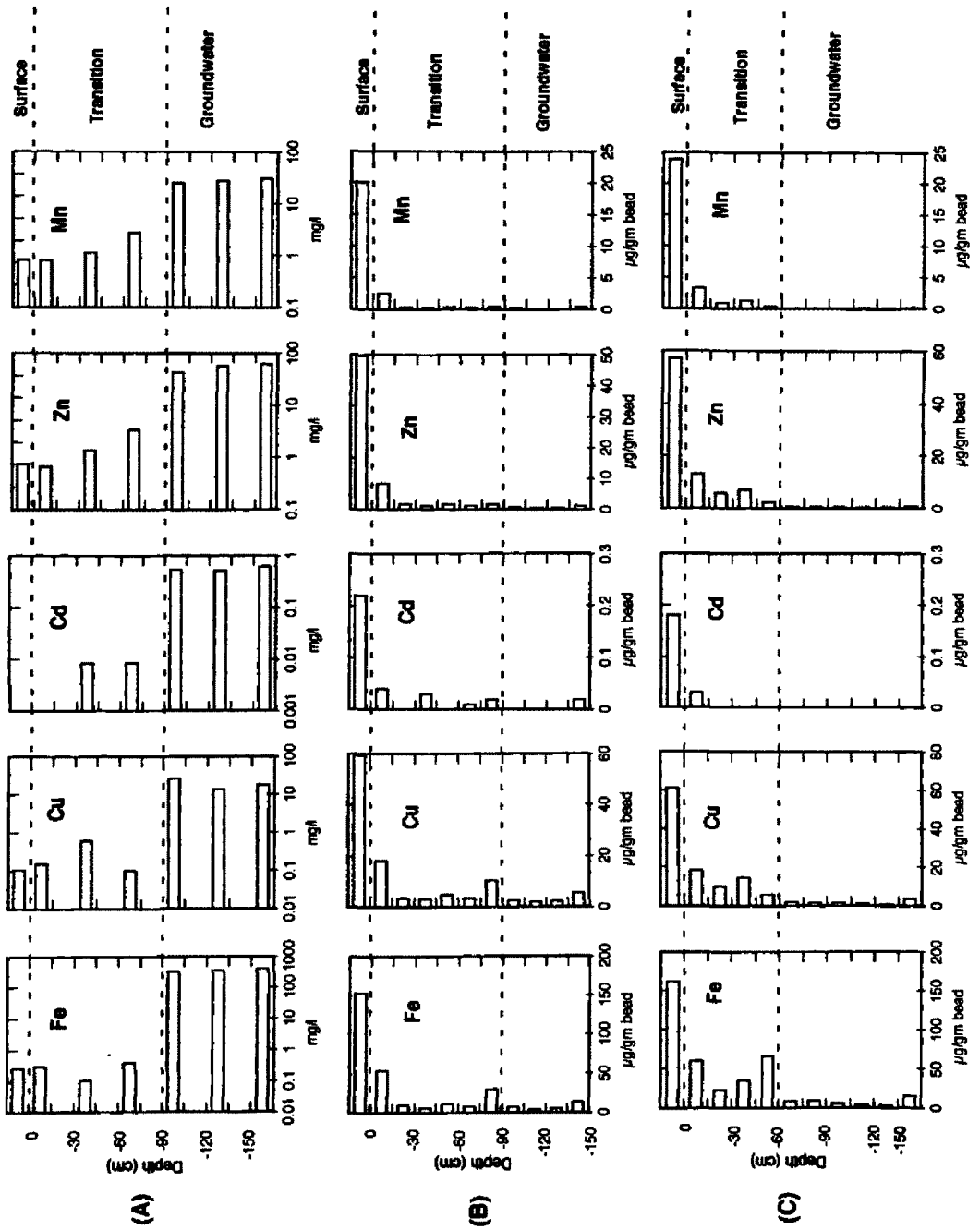


Figure 7b



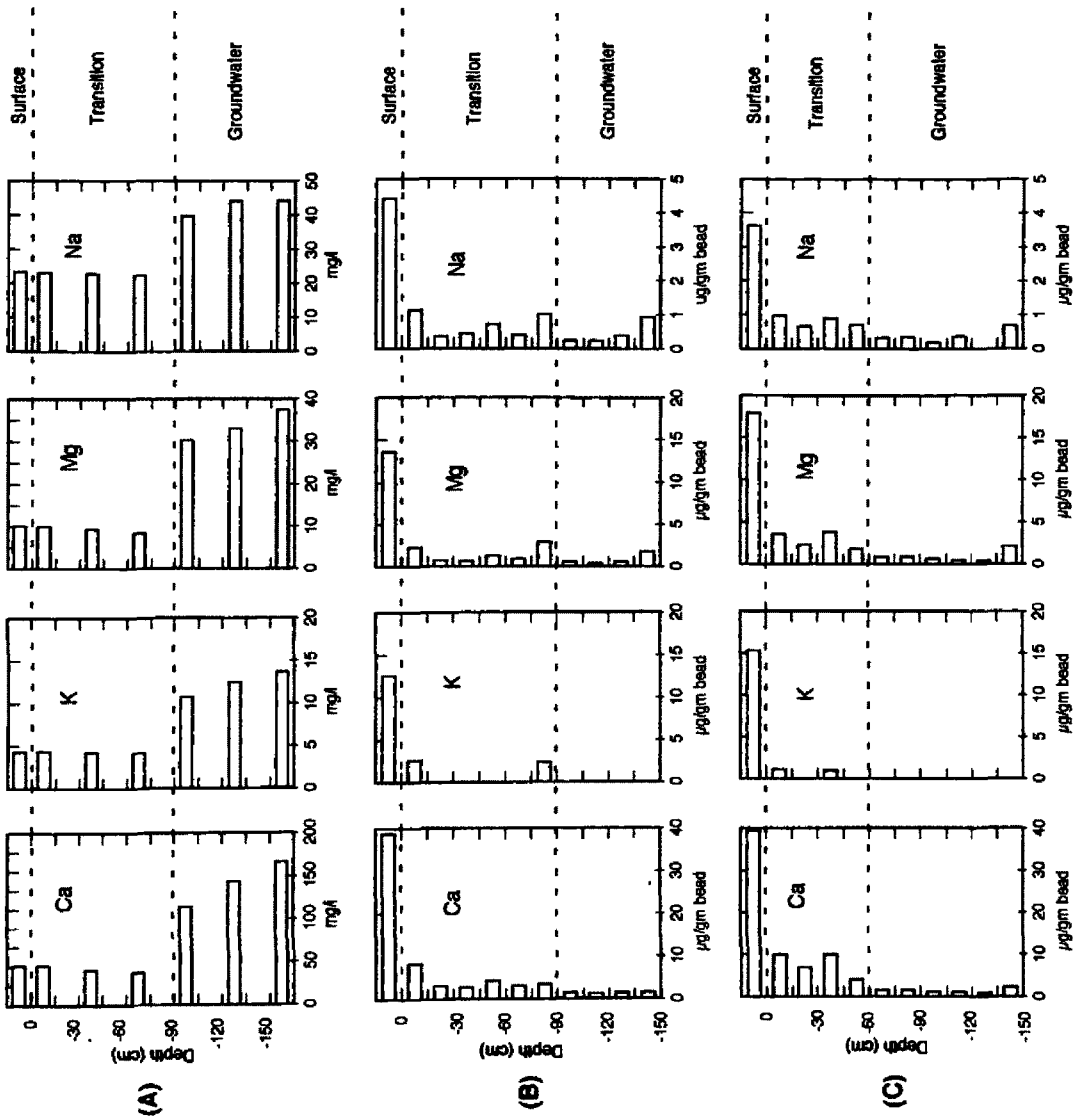
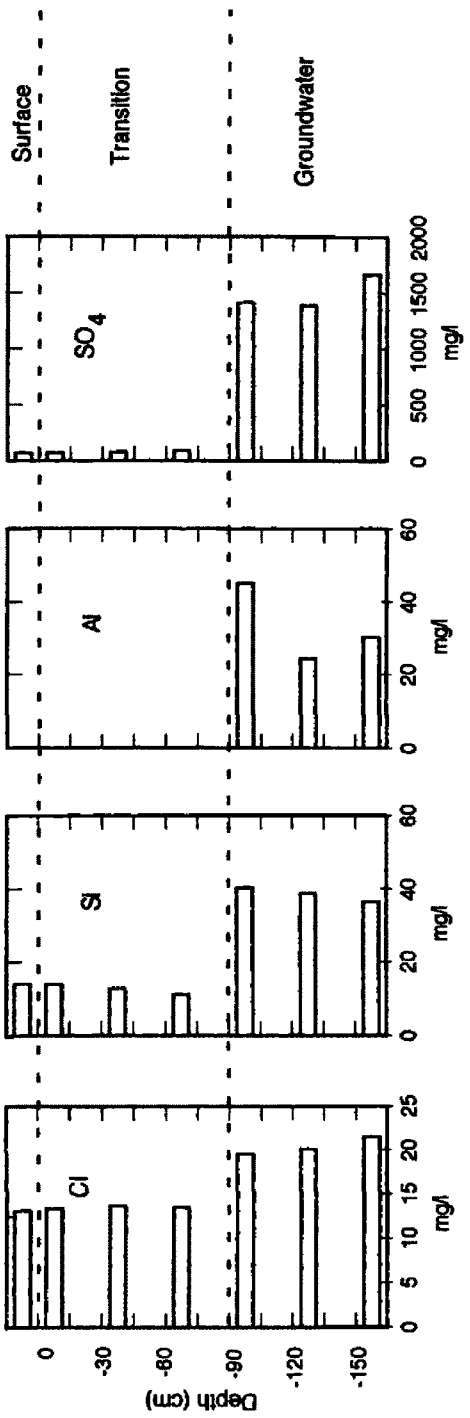


Figure 7d



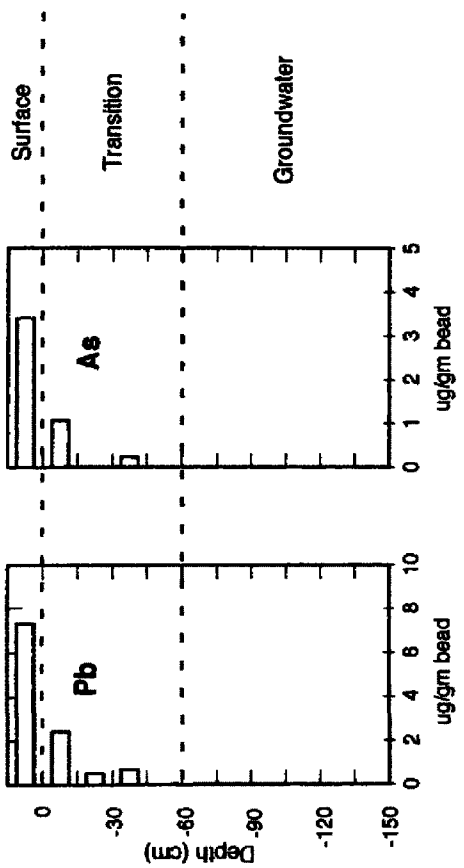
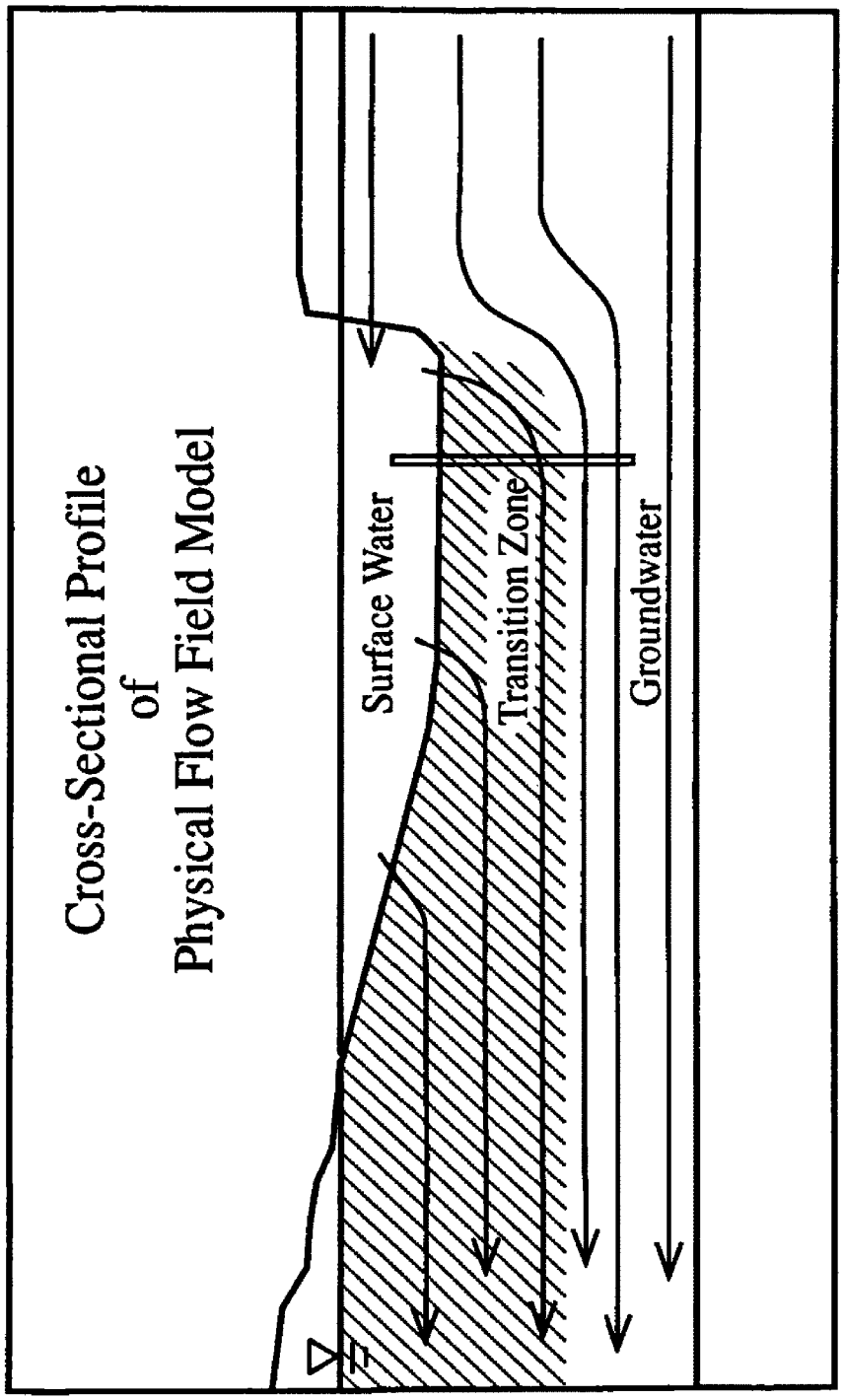


Figure 8



Redox Reaction Sequence

Ref. #	Reaction	Equation
1.	Aerobic respiration	$CH_2O + O_2 = CO_2 + H_2O$
2.	Denitrification	$CH_2O + (4/5)NO^{3-} + (4/5)H^+ = CO_2 + (2/5)N_2 + (7/5)H_2O$
3.	Mn(IV) reduction	$CH_2O + 2MnO_2 + 4H^+ = 2Mn^{2+} + 3H_2O + CO_2$
4.	Fe(III) reduction	$CH_2O + 8H^+ + 4Fe(OH)_3 = 4Fe^{2+} + 11H_2O + CO_2$
5.	Sulfate reduction	$CH_2O + (1/2)SO_4^{2-} + (1/2)H^+ = (1/2)HS^- + H_2O + CO_2$

Carbonate Reaction Sequence

6.	$CO_2 + H_2O = H_2CO_3$
7.	$H_2CO_3 = HCO_3^- + H^+$
8.	$HCO_3^- = CO_3^{2-} + H^+$

Sulfide (pyrite) Oxidation Sequence

9.	$FeS_{2(s)} + (7/2)O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$
10.	$Fe^{2+} + (1/4)O_2 + H^+ = Fe^{3+} + (1/2)H_2O$
11.	$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+$
12.	$FeS_{2(s)} + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

Figure 9

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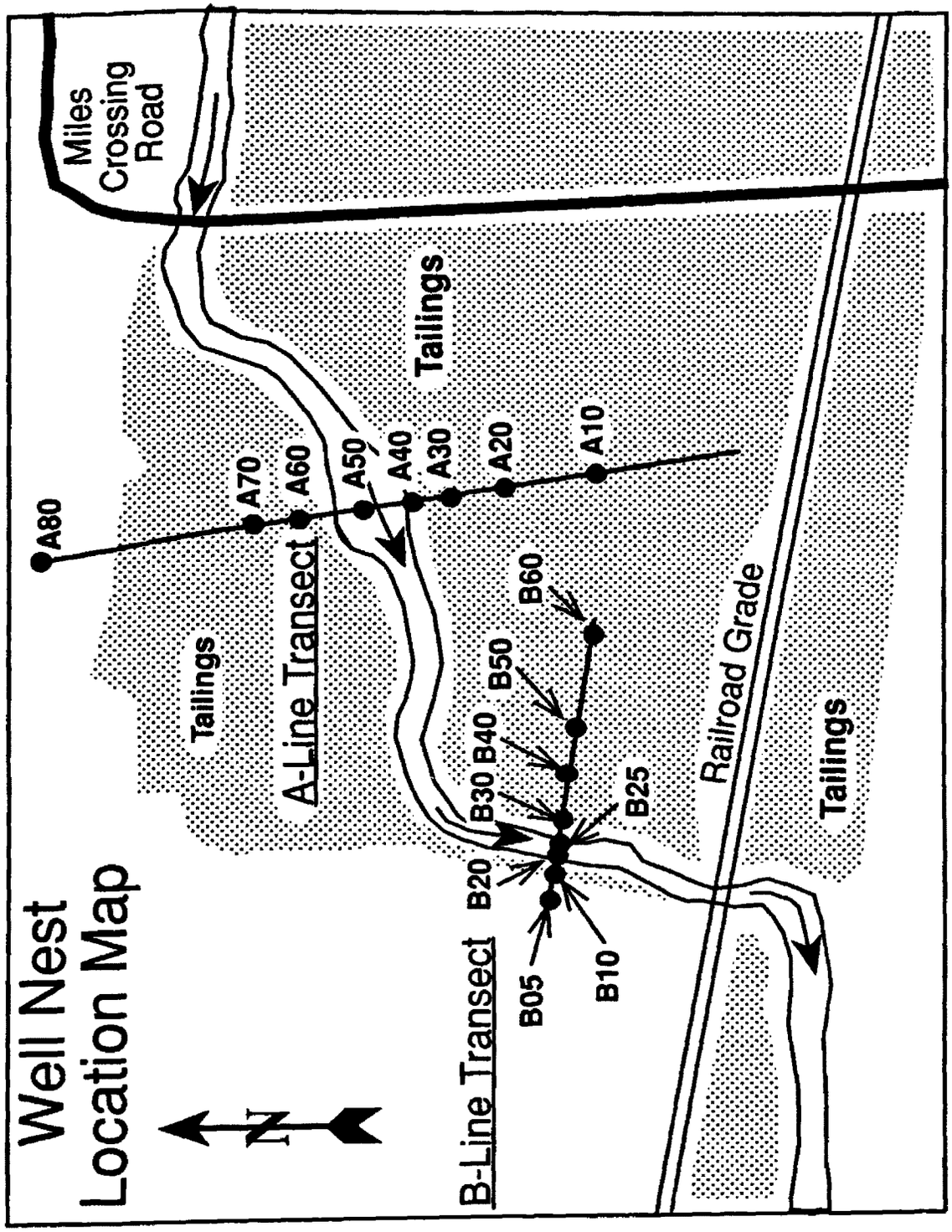
36. Wielinga, B., *et al. Geomicrobial profile through the hyporheic zone in a historic mining flood plain.* in *Second international conference on ground water ecology.* 1994. Atlanta, GA:

Appendix A
(Water Chemistry)

Water Chemistry

Water Chemistry is tabulated with the constituent measured and the date of sampling along the left hand margin, and the well number across the top. Concentrations are in mg/l. All samples were collected during 1993. "BDL" = Below Level of Detection. See attached site map for well locations.



Water Chemistry

Spl. #	DATE	L.O.D.	A10 6.75	A20 5.25	A20 7.25	A20 8.75	A30 2.0	A40 2.7	A40 4.5	A50 3.75	A60 4.5	A70 3.5	A70 4.5	A70 5.5	A80 8.0	ASW	BSW
Al	4.11	0.12	14.3	BDL	0.117	0.208	BDL	BDL	BDL	BDL	0.13				BDL	BDL	BDL
Al	4.25	0.12	5.86	BDL	BDL	BDL	BDL	BDL	0.236	BDL	0.248	1.21	0.157		BDL	BDL	BDL
Al	5.22	0.12	4.61	BDL	BDL	0.179	BDL	BDL	BDL	BDL	BDL	1.79	1.2	0.2	0.132	BDL	BDL
Al	6.17	0.12	1.73	BDL	BDL	BDL	BDL									BDL	
Al	7.13	0.12	1.7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.79	1.34	0.206	BDL	BDL	BDL
Al	8.25	0.12															BDL
Alk.	4.11	2	BDL	40	34	34	84	84	80	68	50				118	96	96
Alk.	4.25	2	14	44	36	32	96	66	72	76	72	18	24		106	94	94
Alk.	5.22	2													106		84
Alk.	6.17	2															
Alk.	7.13	2													120		90
Alk.	8.25	2															
As	4.11	0.12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL				BDL	BDL	BDL
As	4.25	0.12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
As	5.22	0.12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
As	6.17	0.12	BDL	BDL	BDL	BDL	BDL									BDL	
As	7.13	0.12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
As	8.25	0.12															BDL
Ca	4.11	0.027	167	148	159	144	46.4	37.4	43.4	39.3	64.2				65.9	46.2	47.6
Ca	4.25	0.027	164	152	153	147	49.7	46.3	79.2	50.2	68.1	57.2	49.5		62.4	44	46.5
Ca	5.22	0.027	14.2	16.1	15.2	13.8	5.02	8.91	12.3	6.59	7.06	5.69	7.08	4.74	6.19	4.19	4.26
Ca	6.17	0.027	170	159	158	166	49.6									47.3	
Ca	7.13	0.027	187	171	180	174	44	135	177	65.3	74.8	59	64.3	55.7	56.9	45.8	46.2
Ca	8.25	0.027															48.6
Cd	4.11	0.008	0.1277	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL				BDL	BDL	BDL
Cd	4.25	0.008	0.0759	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.2589	BDL		BDL	BDL	BDL
Cd	5.22	0.008	0.0598	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.1449	0.1488	BDL	BDL	BDL	BDL
Cd	6.17	0.008	0.0439	BDL	BDL	BDL	0.0089									BDL	
Cd	7.13	0.008	0.0517	BDL	BDL	BDL	0.0091	BDL	BDL	BDL	BDL	0.1074	0.1081	BDL	BDL	BDL	BDL
Cd	8.25	0.008															BDL
Cl	7.13	5.000	24.3	16.8	16.7	16.7	13.3	19.3	20.7	16.9	17.7	15.7	18.1	19.5	22.8	13.7	13.9
Co	4.11	0.019	0.0287	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL				BDL	BDL	BDL
Co	4.25	0.019	0.0365	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0233	BDL		BDL	BDL	BDL
Co	5.22	0.019	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0313	0.0331	BDL	BDL	BDL	BDL
Co	6.17	0.019	BDL	BDL	BDL	BDL	BDL									BDL	
Co	7.13	0.019	BDL	BDL	BDL	BDL	BDL	BDL	0.0202	BDL	BDL	0.0394	0.033	BDL	BDL	BDL	BDL
Co	8.25	0.019															

Water Chemistry

Sol. #	DATE	L.O.D.	B5 7.25	B10 2.7	B10 4.7	B10 7.5	B20 1.5	B20 2.7	B20 4.7	B30 2.7	B30 4.7	B30 7.5	B40 2.8	B50 6.25	B60 5.5	B60 7.5
Al	4.11	0.12		3.24	0.178			65.8	80.2	60.2	57.2		63.2	8.04		
Al	4.25	0.12		6.49	0.333		BDL	75.1	97.9	89.1	46.7		54.5	8.02		
Al	5.22	0.12	23.7	3.22	0.323		BDL	27.5	43.3	80.5	46.7		32.4	7.55	BDL	BDL
Al	6.17	0.12								99.7			65.7		BDL	
Al	7.13	0.12	41.1	1.83	0.219		BDL	29.8	56	91.1	99.8		67.6	6.92	BDL	BDL
Al	8.25	0.12	53.2	0.438	0.307	19.9		17.5	58.5	67.2	75	43.1	69.9	10.5	BDL	BDL
Alk.	4.11	2		14	46			BDL	BDL	BDL	BDL		BDL	4.76		
Alk.	4.25	2		BDL	52		82	BDL	BDL	BDL	82		BDL	BDL		
Alk.	5.22	2	BDL				86	BDL	BDL							53
Alk.	6.17	2														
Alk.	7.13	2					90	4	BDL							
Alk.	8.25	2											BDL	10	50	
As	4.11	0.12		BDL	BDL			BDL	BDL	BDL	BDL		BDL	BDL		
As	4.25	0.12		BDL	BDL		BDL	BDL	BDL	BDL	BDL		BDL	BDL		
As	5.22	0.12	BDL	BDL	BDL		BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL	BDL
As	6.17	0.12								BDL			BDL		BDL	
As	7.13	0.12	BDL	BDL	BDL		BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL	BDL
As	8.25	0.12	BDL	BDL	BDL	BDL		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ca	4.11	0.027		79.3	74.5			107	134	87.4	87.5		94.1	104		
Ca	4.25	0.027		76	75.2		44.6	105	126	89.2	76.1		76.6	101		
Ca	5.22	0.027	14.4	5.59	6.94		4.52	7.48	8.46	9.62	8.19		6.69	11.9	19.5	13.5
Ca	6.17	0.027								132			117		170	
Ca	7.13	0.027	129	44.2	44.9		44.1	92.5	105	130	134		130	83.9	189	166
Ca	8.25	0.027	132	38.9	44.3	115		94	106	99.7	104	168	119	87.2	169	182
Cd	4.11	0.008		0.1718	0.0779			0.4293	0.5735	0.5344	0.6966		0.6471	2.029		
Cd	4.25	0.008		0.1178	0.0832		BDL	0.4735	0.5663	0.2792	0.5142		0.5027	1.358		
Cd	5.22	0.008	0.3821	0.074	0.0767		BDL	0.3125	0.4168	0.4569	0.4823		0.4087	1.584	BDL	BDL
Cd	6.17	0.008								0.4602			0.6495		BDL	
Cd	7.13	0.008	0.5048	0.047	0.0516		BDL	0.3764	0.6055	0.3237	0.5469		0.5876	1.556	BDL	BDL
Cd	8.25	0.008	0.6547	0.0244	0.0596	0.8902		0.2831	0.6085	0.2046	0.3327	1.027	0.3533	0.8946	BDL	BDL
Cl	7.13	5.000	18.8	14.4	15.2		14.4	20.9	23.4	14.4	20.7		15.4	22.7	19.7	19.7
Co	4.11	0.019		0.0405	BDL			0.2013	0.2748	0.1614	0.1548		0.1746	0.0684		
Co	4.25	0.019		0.0444	BDL		BDL	0.2086	0.2592	0.2267	0.1358		0.1394	0.0495		
Co	5.22	0.019	0.202	0.0901	0.0241		BDL	0.1055	0.168	0.1916	0.1614		0.1006	0.0816	BDL	BDL
Co	6.17	0.019								0.2169			0.1718		BDL	
Co	7.13	0.019	0.209	0.0212	BDL		BDL	0.1106	0.1875	0.2164	0.2415		0.181	0.0791	BDL	BDL
Co	8.25	0.019	0.2214	BDL	BDL	0.1989		0.0735	0.181	0.1507	0.1844	0.3087	0.175	0.0749	BDL	BDL

Water Chemistry

Spl. #	DATE	L.O.D.	A10 6.75	A20 5.25	A20 7.25	A20 8.75	A30 2.0	A40 2.7	A40 4.5	A50 3.75	A60 4.5	A70 3.5	A70 4.5	A70 5.5	A80 8.0	ASW	BSW
Cu	4.11	0.021	26.27	BDL	0.0725	0.0615	0.0335	BDL	BDL	0.0712	0.0328				0.0266	0.0385	0.0448
Cu	4.25	0.021	16.7	0.032	0.0227	BDL	0.1282	BDL	0.1925	0.1246	0.1246	0.1508	BDL		BDL	0.0515	0.083
Cu	5.22	0.021	13.52	BDL	0.053	0.0721	0.1702	BDL	BDL	0.0954	BDL	4.109	0.7742	BDL	0.0731	0.0666	0.0637
Cu	6.17	0.021	9.322	BDL	BDL	BDL	0.3954									0.1859	
Cu	7.13	0.021	9.356	BDL	BDL	BDL	0.499	BDL	BDL	0.0571	BDL	4.35	0.7573	BDL	BDL	0.0642	0.0539
Cu	8.25	0.021															0.1297
DO	4.11		0	0.3	0.9	0.3	0	0.2	0.2	0.2	0.2				0	12.8	3.3
DO	4.25		0.1	0.1	0.3	0.1	0.1	0.4	0.3	0.1	0.1	0.1	0.1		0.2	11.8	11.5
D.O.	5.22		0	0.1	0.4	0.5	0.1	0.1	0.4	0.1	0.1	0.1	0.1	0.6	0.2	9	9
D.O.	6.17		0.5	0.5	0.7	0.8	0.4									5.9	
D.O.	7.13		0.4	0.2	0.6	0.5	0.2	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	10.9	10.4
D.O.	8.25																
Fe	4.11	0.027	20.9	15	13.1	18.5	0.033	5.74	4.17	1.43	14.5				0.078	0.06	0.107
Fe	4.25	0.027	27.1	15.8	12.8	17.9	0.216	6.71	9.19	2.03	15.8	10.2	10.2		0.074	0.318	0.148
Fe	5.22	0.027	24.9	16.5	12.3	16.6	BDL	11.1	11	2.12	14.4	8.65	11.7	9.36	1.29	0.199	0.134
Fe	6.17	0.027	26.5	15	12.9	19.7	BDL									0.298	
Fe	7.13	0.027	29.8	16.1	14.7	20.2	BDL	16.3	15.5	1.83	15.3	9.07	9.6	11.1	BDL	BDL	BDL
Fe	8.25	0.027															0.166
K	7.13	1															
K	8.25	1															4.465
Mg	4.11	0.14	44	35.6	36	33.8	9.56	9.67	11.2	8.72	14.3				16.1	9.72	9.32
Mg	4.25	0.14	50.7	41.6	40.1	38.2	10.9	13.5	23.1	12.7	14.5	11.9	11.9		15	8.19	10.6
Mg	5.22	0.14	4.16	4.37	3.71	3.57	1.13	2.44	3.42	1.56	1.64	1.19	1.46	1.12	1.71	0.904	0.884
Mg	6.17	0.14	54.2	40.8	39.2	43.7	10.4									9.62	
Mg	7.13	0.14	58.3	43.2	43.5	42.6	8.57	34.4	45.5	13.8	15.7	12.1	13.5	13.2	16.2	9.76	9.44
Mg	8.25	0.14															10.8
Mn	4.11	0.005	50.9	10.75	12.89	19.76	1.377	7.591	7.923	1.643	3.217				3.412	0.7426	0.7186
Mn	4.25	0.005	44.4	11.81	12.75	20.79	1.52	10.09	14.76	1.941	3.361	4.161	3.197		3.258	0.5872	0.8017
Mn	5.22	0.005	34.94	12.54	12.07	19.22	1.674	18.57	22.66	2.158	3.567	4.591	4.958	2.956	3.548	0.5479	0.5679
Mn	6.17	0.005	41.35	11.94	12.07	23.68	1.562									1.037	
Mn	7.13	0.005	46.04	13.12	13.54	23.83	1.395	27.9	31.62	2.034	3.714	4.598	4.547	3.535	3.179	0.6576	0.5731
Mn	8.25	0.005															0.937
Mo	4.11	0.018	0.0392	0.0238	0.0252	0.0204	BDL	BDL	BDL	BDL	0.0259				BDL	BDL	BDL
Mo	4.25	0.018	0.0556	BDL	BDL	0.0296	BDL	0.0256	0.0239	BDL	0.0228	0.0252	0.0204		BDL	BDL	BDL
Mo	5.22	0.018	0.0312	0.0289	0.0193	0.0465	BDL	0.0386	0.0327	0.0208	0.0221	BDL	BDL	0.0196	BDL	BDL	BDL
Mo	6.17	0.018	0.0418	0.0289	0.0234	0.0335	BDL									BDL	
Mo	7.13	0.018	0.0447	0.0271	0.0253	0.0339	BDL	0.0326	0.0281	0.0183	0.0261	BDL	0.0196	0.0242	BDL	BDL	BDL
Mo	8.25	0.018															

Water Chemistry

Spl. #	DATE	L.O.D.	B5 7.25	B10 2.7	B10 4.7	B10 7.5	B20 1.5	B20 2.7	B20 4.7	B30 2.7	B30 4.7	B30 7.5	B40 2.8	B50 6.25	B60 5.5	B60 7.5
Cu	4.11	0.021		7.584	0.8036			40.1	47.64	37.03	28.86		38.27	1.526		
Cu	4.25	0.021		9.785	1.234		0.0608	44.63	57.08	55.58	26.03		34.09	1.236		
Cu	5.22	0.021	9.165	6.337	1.221		0.1524	23.93	34.18	59.05	30.89		23.59	0.9808	BDL	BDL
Cu	6.17	0.021								47.81			39.9		BDL	
Cu	7.13	0.021	17.06	3.79	0.6898		0.0989	24.28	39.87	48.78	52.62		39.74	1.574	BDL	BDL
Cu	8.25	0.021	24.39	1.291	0.9903	13.12		16.52	39.52	30.75	41.82	17.39	39.47	6.507	BDL	BDL
DO	4.11			0.3	1.6			0.9	0.3	0.5	0.2		0.3	0		
DO	4.25			0.1	0.1		1.3	0	0.2	0.4	1.3		0.1	0.1		
D.O.	5.22		0	0.3	0.5		1.7	0.1	0	0	0.1		0	0.2	0.1	0.2
D.O.	6.17									0.4			0.3			
D.O.	7.13		0.2	0.1	0.1		6.3	0.1	0.3	0.1	0.2		0.1	0.2	0.1	0.1
D.O.	8.25															
Fe	4.11	0.027		50.1	5.47			387	510	280	299		290	137		
Fe	4.25	0.027		58.8	7.88		0.05	372	486	361	256		231	114		
Fe	5.22	0.027	282	40.9	6.97		0.136	186	296	317	267		171	139	23.1	18.8
Fe	6.17	0.027								389			320		20.5	
Fe	7.13	0.027	323	28.8	4.31		0.031	197	347	402	440		328	144	22.2	24.6
Fe	8.25	0.027	361	10.4	5.16	318		138	359	384	392	556	341	138	21.4	27.2
K	7.13	1														
K	8.25	1	11.83	5.85	7.26	12		9.497	12.84	3.564	9.138	17.6	6.48	9.893	11.8	11.66
Mg	4.11	0.14		17	14.7			27.9	34	23.7	23.8		24.9	22.8		
Mg	4.25	0.14		18.5	17		10	30.6	37.9	30.3	22.1		22	26.4		
Mg	5.22	0.14	3.22	1.31	1.52		0.952	2.06	2.38	3.11	2.36		1.87	2.97	5.21	3.39
Mg	6.17	0.14								38.6			32.6		45.3	
Mg	7.13	0.14	32.3	10.5	9.9		9.19	23.1	29.4	39	39.7		35.5	20.2	50	41.6
Mg	8.25	0.14	35.5	8.95	10.1	28		22.7	30.6	30.2	32.4	41.9	33.7	23.4	46.7	48.6
Mn	4.11	0.005		5.995	3.694			23.75	30.62	20.46	22.08		22.98	17.61		
Mn	4.25	0.005		6.112	4.266		0.5035	25.17	31.1	32.3	18.97		19.07	18.26		
Mn	5.22	0.005	19.97	4.309	3.888		0.5756	14.74	19.57	31.56	21.04		15.26	20.49	34.61	22.26
Mn	6.17	0.005								38			27.25		29.42	
Mn	7.13	0.005	19.08	3.374	2.494		0.6754	14.83	24	37.94	37.76		29.95	14.88	31.48	26.96
Mn	8.25	0.005	21.08	2.252	2.6	21.97		10.69	24.54	30.27	34.23	33.15	30.91	17.28	29.94	30.3
Mo	4.11	0.018		0.0697	BDL			0.5454	0.7139	0.3919	0.417		0.4057	0.1945		
Mo	4.25	0.018		0.0925	0.02		BDL	0.518	0.6663	0.5021	0.356		0.3257	0.166		
Mo	5.22	0.018	0.4039	0.0553	BDL		BDL	0.267	0.419	0.4528	0.3809		0.2397	0.1934	0.038	0.0309
Mo	6.17	0.018								0.5478			0.4505		0.0335	
Mo	7.13	0.018	0.4519	0.0444	BDL		BDL	0.2754	0.4853	0.5641	0.6169		0.4616	0.2041	0.0366	0.042
Mo	8.25	0.018	0.5027	BDL	BDL	0.4402		0.1942	0.4974	0.5318	0.5425	0.7685	0.4735	0.1902	0.0352	0.0441

Water Chemistry

Spl. #	DATE	L.O.D.	A10 6.75	A20 5.25	A20 7.25	A20 8.75	A30 2.0	A40 2.7	A40 4.5	A50 3.75	A60 4.5	A70 3.5	A70 4.5	A70 5.5	A80 8.0	ASW	BSW
Na	4.11	0.063	73.3	71	69.1	64.8	20.4	32.1	34.4	22.5	28				97.5	20	19.4
Na	4.25	0.063	95.8	88.2	83.9	76.4	24.1	42.4	53.7	29.9	26.9	22.5	24.3		94.5	17.2	23.8
Na	5.22	0.063	80.1	93.4	75	71.6	25.5	53.2	59.7	28.2	32.5	21.9	25.3	25.2	121	23.4	23.1
Na	6.17	0.063	108	85.1	82.4	89	22									21.1	
Na	7.13	0.063	115	90.2	91.1	85.4	20.8	63.7	72.9	26.2	31.4	27.7	27.7	28.3	121	23.1	21.8
Na	8.25	0.063															25
Ni	4.11	0.054	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL				BDL	BDL	BDL
Ni	4.25	0.054	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
Ni	5.22	0.054	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	6.17	0.054	BDL	BDL	BDL	BDL	BDL									BDL	
Ni	7.13	0.054	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	8.25	0.054															*BDL*
P	4.11	0.18	*3.4*	*1.1*	*1.3*	*1.3*	*0.75*	*0.96*	*1.2*	*0.91*	*0.77*				*1.6*	*0.69*	1.2
P	4.25	0.18	0.75	0.27	0.32	1	0.74	0.18	0.48	BDL	1.2	0.45	0.32		1.7	1.8	0.31
P	5.22	0.18	1.7	BDL	0.97	0.95	BDL	0.97	0.8	0.78	0.61	BDL	0.67	0.7	0.61	0.35	0.76
P	6.17	0.18	0.33	0.47	0.49	0.32	0.27									0.35	
P	7.13	0.18	0.56	0.48	0.52	0.49	0.41	0.5	0.52	0.39	0.57	BDL	BDL	0.36	0.21	BDL	0.3
P	8.25	0.18															BDL
Pb	4.11	0.18	0.425	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL				BDL	BDL	BDL
Pb	4.25	0.18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
Pb	5.22	0.18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb	6.17	0.18	BDL	BDL	BDL	BDL	BDL									BDL	
Pb	7.13	0.18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb	8.25	0.18															BDL
pH	4.11		5.44	6.77	6.65	6.79	7.2	6.8	6.82	6.68	6.53				7	8.18	8
pH	4.25		6.54	7.23	7.2	7.05	7.59	7.15	7.08	6.96	6.89	5.9	6.43		7.52	9.09	8.98
pH	5.22		6.12	6.85	6.81	6.8	7.19	6.73	6.65	6.62	6.58	5.34	5.58	6.25	7.13	8.18	8.49
pH	6.17		6.34	6.83	6.78	6.51	7									7.72	
pH	7.13		6.39	6.78	6.78	6.55	6.92	6.59	6.45	6.59	6.36	5.05	5.46	5.85	7.1	8.17	8.58
pH	8.25																7.9
Si	4.11	0.036	30.2	23.1	25.2	25.9	9.5	16	16.1	6.25	15.8				16.2	11.7	11.9
Si	4.25	0.036	32.1	25.2	25.7	27.8	10.9	17.2	18	6.29	15.6	16.6	15.8		15.9	9.98	11.4
Si	5.22	0.036	25.1	22.8	21.7	23.3	9.96	16.9	16	7.57	15.5	15.7	17.1	14.8	16.4	11.4	12.4
Si	6.17	0.036	26.9	24.1	22.9	28.3	11.1									11.5	
Si	7.13	0.036	29.1	25.1	25	28.1	10.8	18.2	18.6	8.26	18.4	19.7	19.4	16.7	17.8	10.2	9.95
Si	8.25	0.036															13.1
SO4	7.13	6	955.7	726.4	744	748.3	81.6	533.1	717.1	143	209.4	240.1	245.6	191.1	275.5	73.7	70.3

Water Chemistry

Spl. #	DATE	L.O.D.	B5 7.25	B10 2.7	B10 4.7	B10 7.5	B20 1.5	B20 2.7	B20 4.7	B30 2.7	B30 4.7	B30 7.5	B40 2.8	B50 6.25	B60 5.5	B60 7.5
Na	4.11	0.063		25.3	25.4			29.9	31	33.4	32.3		32.7	43.4		
Na	4.25	0.063		28.2	28.6		22.5	33.3	37.9	18.5	39.3		33.8	56		
Na	5.22	0.063	32.9	28.9	28.5		24.6	33.5	31.7	42.6	38.6		41.5	63.5	99.9	73.1
Na	6.17	0.063								47.9			53.2		92.3	
Na	7.13	0.063	34.9	24.9	24.2		22.4	37.6	44.7	48.2	48.2		54.2	55	96.9	86.5
Na	8.25	0.063	38.5	25.7	25.8	38.5		34.6	47.1	48.1	44.8	48.4	53	67.6	93	102
Ni	4.11	0.054		BDL	BDL			0.192	0.256	0.142	0.141		0.164	0.079		
Ni	4.25	0.054		BDL	BDL		BDL	0.171	0.198	0.19	0.096		0.12	BDL		
Ni	5.22	0.054	0.201	BDL	BDL		BDL	0.092	0.132	0.162	0.12		0.089	0.064	BDL	BDL
Ni	6.17	0.054								0.181			0.151		BDL	
Ni	7.13	0.054	0.24	BDL	BDL		BDL	0.095	0.161	0.181	0.195		0.156	0.067	BDL	BDL
Ni	8.25	0.054	0.243	BDL	BDL	0.207		0.064	0.151	0.128	0.159	0.3	0.154	0.066	BDL	BDL
P	4.11	0.18		1.8	1.2			3.2	4.5	2.7	2.1		3.2	1.4		
P	4.25	0.18		0.97	0.48		0.38	1.9	1.3	6.6	1.5		2.4	BDL		
P	5.22	0.18	0.94	0.82	0.58		0.47	0.53	1.6	2.5	1.4		1.4	0.33	0.35	0.97
P	6.17	0.18								1.4			1.3		0.39	
P	7.13	0.18	0.47	0.22	BDL		0.19	0.64	1	1.4	1.3		1	BDL	0.37	0.48
P	8.25	0.18	0.64	0.32	BDL	0.29		0.51	1.1	1	1.1	0.47	0.92	BDL	0.31	0.33
Pb	4.11	0.18		BDL	BDL			BDL	0.183	0.258	1.43		BDL	BDL		
Pb	4.25	0.18		BDL	BDL		BDL	BDL	BDL	BDL	1.42		BDL	BDL		
Pb	5.22	0.18	BDL	BDL	BDL		BDL	BDL	BDL	0.43	1.64		BDL	BDL	BDL	BDL
Pb	6.17	0.18								0.509			BDL		BDL	
Pb	7.13	0.18	BDL	BDL	BDL		BDL	BDL	BDL	0.499	2.14		BDL	BDL	BDL	BDL
Pb	8.25	0.18	BDL	BDL	BDL	BDL		BDL	BDL	0.356	1.94	BDL	BDL	BDL	BDL	BDL
pH	4.11			5.55	6.32			4.47	4.18	4.31	4.36		4.02	4.76		
pH	4.25			6	6.64		7.57	4.77	4.62	3.6	7.57		4.38	5.2		
pH	5.22		4.8	5.86	6.2		7.25	4.87	4.35	3.52	4.49		3.9	4.96	6.71	7.16
pH	6.17									3.4			3.78			
pH	7.13		4.35	5.91	6.24		7.23	4.72	4.18	3.35	4.1		3.7	4.64	6.41	6.55
pH	8.25		4.2	5.96	6.06	4.73		4.93	4.08	3.37	4.11	4.33	3.82	4.43	6.15	6.32
Si	4.11	0.036		13.3	9.16			36.6	43.2	41.5	38.1		42.7	22.3		
Si	4.25	0.036		15.6	9.93		10.4	39.7	45.8	32.6	36.3		37.8	22.2		
Si	5.22	0.036	20	15.8	10.8		12.5	31.1	35.4	55.5	39.1		30.8	21.6	27.3	20.6
Si	6.17	0.036								63.7			47.5		29.3	
Si	7.13	0.036	26.7	12.2	10.2		10	31.3	42.8	65.5	52		47.6	23.3	26.8	24.4
Si	8.25	0.036	34.1	14.4	11	32.6		25.5	42.8	68.9	59.8	47.1	61.1	26.5	28.4	28.4
SO4	7.13	6	1414.8	193.7	138.2		71.3	894.4	1435	1868.6	1980.7		1598.3	690.1	864.4	769.1

Water Chemistry

Spl. #	DATE	L.O.D.	A10 6.75	A20 5.25	A20 7.25	A20 8.75	A30 2.0	A40 2.7	A40 4.5	A50 3.75	A60 4.5	A70 3.5	A70 4.5	A70 5.5	A80 8.0	ASW	BSW
Sr	4.11	0.002	0.7035	0.6389	0.6664	0.6551	0.2155	0.2033	0.2311	0.1753	0.3295				0.3189	0.2124	0.2002
Sr	4.25	0.002	0.8691	0.7822	0.7743	0.7536	0.2499	0.2968	0.4874	0.2555	0.3298	0.2849	0.2931		0.3005	0.1781	0.2348
Sr	5.22	0.002	0.7007	0.8446	0.7304	0.7315	0.2699	0.5341	0.7429	0.3251	0.3996	0.2872	0.355	0.2769	0.3701	0.2281	0.227
Sr	6.17	0.002	0.9102	0.7668	0.7526	0.8977	0.2479									0.2328	
Sr	7.13	0.002	0.9798	0.8272	0.8506	0.878	0.2041	0.7526	0.9809	0.2934	0.3826	0.2925	0.3226	0.3222	0.3398	0.2317	0.2242
Sr	8.25	0.002															0.2547
Temp	4.11		1.8	1.6	1.6	1.8	1.2	3.6	3.4	-1.2	-0.7				1.4	4.1	3.6
Temp	4.25		2.9	2.4	2.7	2.6	3.2	5.7	5.6	-0.8	0	-0.6	0.2		2.3		7.1
Temp	5.22		4.1	3.2	3.5	3.1	5.3	8.2	7.6	5.9	2.6	3.9	3.5	2.4	3.6	9.6	10.2
Temp	6.17		6.1	5.3	5.3		8.2									9.8	
Temp	7.13		7	6.2	6.2	6.4	9.1	9.7	8.9	9.1	7	8	7.6	6.5	5.7	11.9	14.1
Temp	8.25																
Ti	4.11	0.007	0.0615	0.0405	0.0476	0.0522	0.0279	0.0315	0.0449	0.0347	0.0282				0.066	0.0217	0.0407
Ti	4.25	0.007	0.0283	0.0127	0.0201	0.0712	0.0507	BDL	0.0308	BDL	0.043	0.0356	0.0125		0.0671	0.0735	0.0185
Ti	5.22	0.007	0.0946	BDL	0.0592	0.0599	BDL	0.0623	0.0517	0.0599	0.035	BDL	0.0444	0.0351	0.0322	BDL	0.0394
Ti	6.17	0.007	BDL	0.0156	0.0189	0.0103	0.0141									0.016	
Ti	7.13	0.007	BDL	0.0107	0.0139	0.0156	0.0151	0.018	0.0193	0.0199	0.0217	BDL	BDL	BDL	BDL	BDL	0.0149
Ti	8.25	0.007															BDL
Zn	4.11	0.006	47.41	0.3777	4.197	2.641	0.943	1.985	3.419	0.4562	2.386				0.7587	0.3542	0.476
Zn	4.25	0.006	23.84	0.3784	2.936	2.456	1.295	2.401	6.213	0.4012	2.509	8.76	3.135		0.7544	0.1859	0.3407
Zn	5.22	0.006	15.52	0.3453	2.215	1.949	1.445	4.492	8.955	0.3367	2.295	9.881	9.702	2.768	0.8871	0.2636	0.2856
Zn	6.17	0.006	14.09	0.1881	1.122	2.486	2.369									1.018	
Zn	7.13	0.006	16.35	0.1409	0.9705	2.043	2.197	6.601	12.84	0.2558	2.594	9.796	8.737	3.166	0.4893	0.4025	0.1988
Zn	8.25	0.006															0.5465

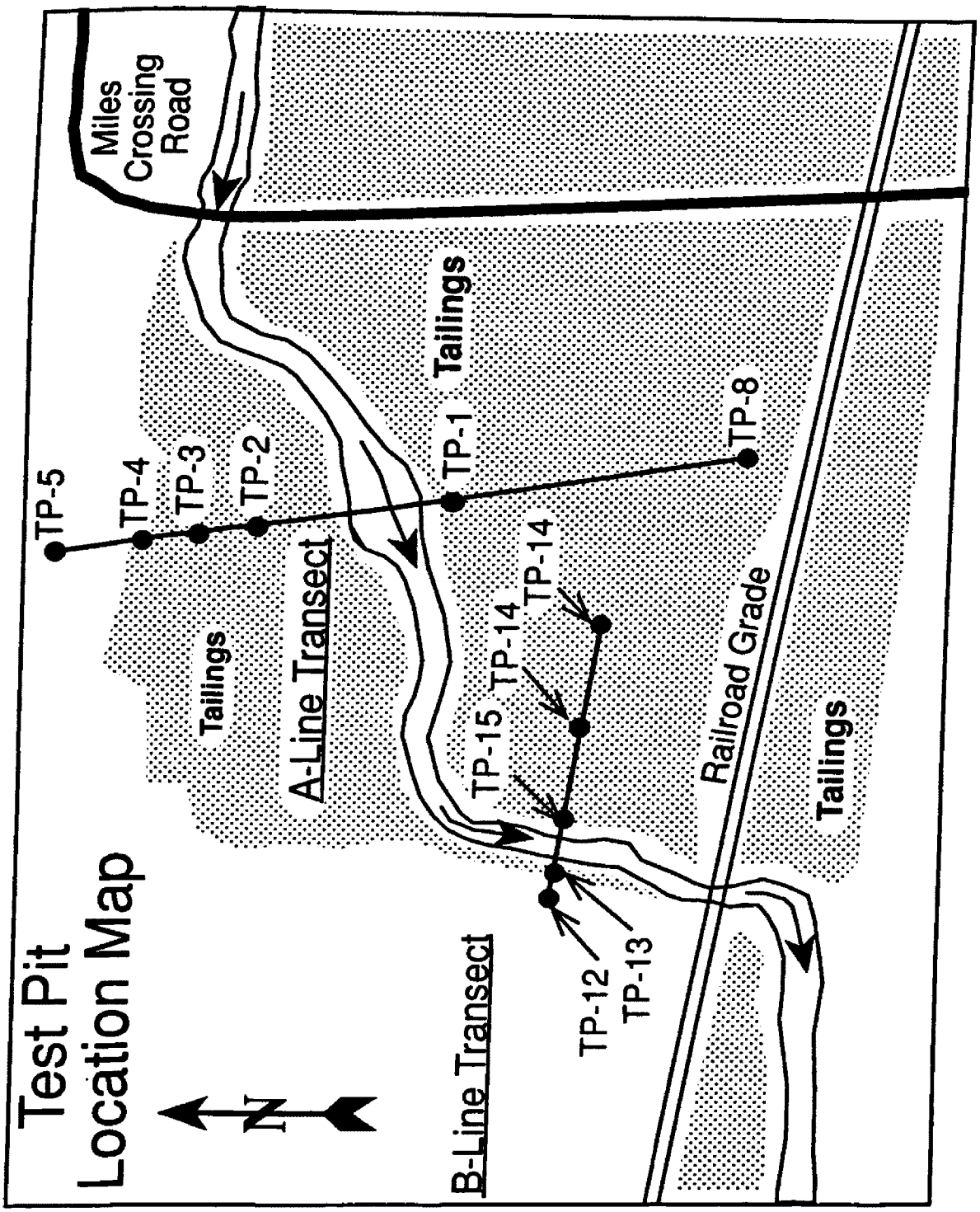
Water Chemistry

Spl. #	DATE	L.O.D.	B5 7.25	B10 2.7	B10 4.7	B10 7.5	B20 1.5	B20 2.7	B20 4.7	B30 2.7	B30 4.7	B30 7.5	B40 2.8	B50 6.25	B60 5.5	B60 7.5
Sr	4.11	0.002		0.2914	0.2954			0.4011	0.4911	0.2868	0.332		0.2777	0.4525		
Sr	4.25	0.002		0.3288	0.349		0.2204	0.4334	0.5726	0.1299	0.3317		0.2532	0.5439		
Sr	5.22	0.002	0.6979	0.2547	0.3237		0.2335	0.3459	0.3777	0.2686	0.3462		0.262	0.6413	1.096	0.6572
Sr	6.17	0.002								0.3794			0.4308		0.942	
Sr	7.13	0.002	0.6481	0.204	0.2109		0.2175	0.4265	0.4832	0.4352	0.5587		0.5082	0.4556	1.042	0.8036
Sr	8.25	0.002	0.7038	0.1793	0.2174	0.6201		0.4618	0.5177	0.3702	0.4709	0.922	0.4741	0.4784	0.9629	0.9482
Temp	4.11			2.3	2.6			3.5	3.2	-1.6	-0.7		-1.3	0.9		
Temp	4.25			4	4		5.8	5.6	5.6	-0.9	5.8		-0.6	2		
Temp	5.22		3.8	9.3	7.6		10.1	8.7	8.1	6.4	4.5		5.5	2.9	2.6	2.7
Temp	6.17									8.1			7.3			
Temp	7.13		5.5	10.5	9.3		12.4	10.9	9.2	9.3	8.3		9.2	5.1	6.3	5.8
Temp	8.25		7.6	11.7	11.2	9.8		11.5	10.8	10.8	9.9	8.4	9	7.1	7.7	6.8
Ti	4.11	0.007		0.053	0.0451			0.0457	0.0649	0.0366	0.0339		0.0465	0.0585		
Ti	4.25	0.007		0.0555	0.0348		0.0275	0.0657	0.0233	0.0868	0.0687		0.1053	0.0151		
Ti	5.22	0.007	0.0536	0.0468	0.0384		0.0221	0.0111	0.0678	0.0365	0.0565		0.0607	0.0284	0.012	0.0623
Ti	6.17	0.007								0.0172			0.0223		0.0128	
Ti	7.13	0.007	0.008	0.0074	BDL		BDL	0.0083	0.0087	0.0095	0.0099		0.009	BDL	0.0074	0.014
Ti	8.25	0.007	BDL	BDL	BDL	BDL		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn	4.11	0.006		9.759	5.34			40.91	56.07	34.81	38.4		41.36	29.84		
Zn	4.25	0.006		8.45	5.829		0.6351	41.59	50.01	47.9	31.88		34.22	25.19		
Zn	5.22	0.006	47.13	5.293	4.901		0.4861	22.73	32.24	44.91	32.53		25.11	30.24	12.87	7.043
Zn	6.17	0.006								51.69			40.85		9.813	
Zn	7.13	0.006	39.19	3.744	3.234		0.4309	23.68	38.29	49.3	49.66		41.47	25.86	9.856	6.945
Zn	8.25	0.006	40.76	2.157	3.649	42.52		17.53	39.67	38.97	41.86	67.91	41.54	25.53	9.912	7.624

Appendix B
(Sediment Chemistry)

Sediment Chemistry

Thirty-six soil samples were obtained by hand from test pits along a transect roughly parallel to well nests (See attached location map). Samples were dried at 70 degrees Celsius for 24 hours. A partial HCl extract was used to approximate metals available to the environment(Luoma and Davis, 1983). Approximately 2.000 gm sediment were digested in 200 ml 0.6 N HCl, shaken for 8 hours, and decanted for analysis. The resulting solution was analyzed for cations using a Thermo-Jarrel Ash ICP. Results are reported in ug/gm sediment. "BDL" indicates element is present at concentrations below the detection limit. "Unit" refers to the stratigraphic unit from which the sample was taken: qtf; fine-grained tailings, qtc; coarse-grained tailings, qpf; fine-grained pre-tailings, qpc; coarse-grained pre-tailings.



Sediment chemistry

sample#	Depth(cm)	unit	Ag	Al	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Mo	Na	P
LOD	-	-	2	10	10	2	0.6	2	2	80	11	0.4	1	5	14
TP1-1a	10	qtf	12	5976	588	1160	6	3639	20400	356	489	1516	33	140	1040
TP1-1b	20	qtf	9	2488	230	797	3	1171	14560	1161	1048	745	23	172	536
TP1-2	40	qtc	7	816	170	570	BDL	363	8480	196	114	316	14	30	280
TP1-3	60	qtc	6	387	217	446	BDL	148	6712	232	76	107	11	44	256
TP1-4	90	qtc	6	362	175	510	BDL	156	8400	313	67	81	13	37	256
TP1-5	110	qtc	BDL	438	14	1088	2	519	4512	181	124	248	6	38	200
TP1-6	130	qpc	5	538	111	781	1	1614	4848	282	134	109	9	30	296
TP8-1	10	qtf	11	4464	424	1776	6	2257	11440	680	690	998	18	154	960
TP8-2	15	qtc	6	888	172	674	BDL	227	7352	338	118	188	13	38	368
TP12-1	10	qtf	BDL	2448	10	1584	4	694	3144	697	952	1060	4	276	360
TP12-2	80	qtc	BDL	1320	BDL	1696	1	141	3856	675	387	337	6	158	528
TP12-3	100	qpc	BDL	526	BDL	1144	1	22	1304	305	143	55	2	56	272
TP13-1	10	qtf	10	2424	195	3992	5	2167	20800	559	676	967	34	99	1440
TP13-2	30	qtf	BDL	2256	168	3488	12	1546	7832	591	606	453	35	104	1040
TP13-3	50	qpc	BDL	1648	61	3864	4	1246	6344	466	360	387	12	91	800
TP14-1	10	qtf	11	4560	274	2296	BDL	1281	10960	623	486	1108	16	135	880
TP14-2	30	qtc	2	2392	126	944	BDL	353	14800	295	89	187	22	36	424
TP14-3	40	qtf	BDL	6056	223	4464	13	2234	14000	886	1008	8064	22	161	1200
TP14-4	80	qtc-crust	2	1416	168	461	BDL	101	52720	230	53	46	76	40	272
TP14-5	90	qpc	5	1456	43	718	BDL	2086	5240	156	50	277	9	36	504
TP15-1	10	qtc	BDL	650	73	515	BDL	60	11280	249	43	28	18	28	680
TP15-2	40	qpc	2	120	BDL	65	BDL	23	2072	304	13	8	3	67	30
TP16-1	140	qpc	4	1016	50	960	BDL	1382	6384	239	188	467	10	83	360
TP16-2	110	qtc	3	241	72	349	BDL	49	6728	221	49	55	10	38	160
TP16-3	80	qtc	7	530	131	602	BDL	116	11200	301	90	151	17	50	272
TP16-4	50	qtc	3	1776	77	666	BDL	354	12080	346	116	134	18	33	304
TP16-5	30	qtf	9	2728	282	1680	1	1126	12160	407	306	340	21	53	688
TP17-1	10	qpf	BDL	3432	18	12400	2	48	1448	2740	6224	464	2	260	512
TP17-2	40	qpf	BDL	3888	BDL	78000	BDL	14	1320	2676	9040	424	2	670	880
TP19-1	30	qtf	3	2912	286	5792	10	2250	16480	717	792	1970	26	263	1520
TP19-2	35	qtf	BDL	3296	225	7448	15	2860	16000	716	791	1632	26	222	2720
TP19-3	60	qpc	BDL	1304	31	758	1	657	3600	207	138	114	7	58	448

Sediment Chemistry

sample#	Depth(cm)	unit	Pb	Si	Sr	Ti	Zn
LOD	-	-	3	3	0.1	0.6	0.5
TP1-1a	10	qtf	1248	2648	13	55	2177
TP1-1b	20	qtf	673	2920	18	102	1164
TP1-2	40	qtc	346	678	3	20	321
TP1-3	60	qtc	284	374	3	21	130
TP1-4	90	qtc	294	442	2	22	141
TP1-5	110	qtc	81	612	4	7	413
TP1-6	130	qpc	250	808	4	13	361
TP8-1	10	qtf	856	2608	19	55	1987
TP8-2	15	qtc	218	563	4	25	299
TP12-1	10	qtf	158	2152	24	82	1383
TP12-2	80	qtc	BDL	1312	14	34	603
TP12-3	100	qpc	BDL	426	6	10	101
TP13-1	10	qtf	976	3384	28	56	1178
TP13-2	30	qtf	638	2160	23	52	3545
TP13-3	50	qpc	408	1656	17	37	1049
TP14-1	10	qtf	936	2384	18	44	513
TP14-2	30	qtc	229	1056	4	12	225
TP14-3	40	qtf	1048	3904	31	79	8208
TP14-4	80	qtc-crust	155	1584	2	13	132
TP14-5	90	qpc	199	816	3	9	236
TP15-1	10	qtc	41	459	2	8	70
TP15-2	40	qpc	53	107	2	35	12
TP16-1	140	qpc	373	1176	6	13	449
TP16-2	110	qtc	71	316	2	10	70
TP16-3	80	qtc	230	628	3	24	118
TP16-4	50	qtc	186	1024	3	20	212
TP16-5	30	qtf	730	1584	11	38	515
TP17-1	10	qpf	22	5624	186	54	348
TP17-2	40	qpf	BDL	6344	465	50	14
TP19-1	30	qtf	1144	2888	42	67	2465
TP19-2	35	qtf	1008	3232	40	68	3237
TP19-3	60	qpc	118	880	4	11	357